Hydrogeochemical assessment of the Mooiplaas dolomite quarry near Laudium in Gauteng, South Africa

by

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Abstract

Karst aquifers within dolomite terrain in South Africa have been researched in the past for dewatering due to gold mining, sinkhole formation, and for its high value to supply sustainable, good quality groundwater. Karst aquifers are also known to be extremely vulnerable therefore, they should be protected and taken care of. Thus, understanding how anthropogenic activity influences the hydrogeochemistry of a karst aquifer is extremely important.

Pretoria Portland Cement Mooiplaas (PPC Mooiplaas) quarry was chosen as the study area because the mining of dolomite, below the natural groundwater level, is a great example of anthropogenic activity within a karst aquifer. There are several factors that influence the movement of the groundwater within the study area such as dykes, faulting and the anthropogenic activity of mining activity itself; such as the plant and the Slimes Dams that produce the product.

The main objectives of the study were to characterise the hydrogeochemistry of the PPC Mooiplaas and to compare the water quality of PPC Mooiplaas to that of it surrounding karst aquifer. To identify the movement of water within the study area by stable isotope analysis and to identify the source of water within the study area. Then lastly it is to understand how the anthropogenic activity impacts the karst aquifer This was carried out by sampling several sites of groundwater (West Pit Seep, Exploration Borehole North, Exploration Borehole South, West Pit Wall Seep, East Pit Wall Seep, Groundwater Flow 1 and Groundwater Flow 12); surface water (West Pit, East Pit and Fish Dam); mine water (Plant Inlet, Slurry Dam, Metallurgical Grade "Vergryser" Slurry Dam and Slimes Dam); and rainwater.

The water samples that were collected at PPC Mooiplaas were tested for major inorganic chemistry and stable isotopes. Due to several factors that influence the water, it is possible to use water chemistry and stable isotopes to gain an understanding of the source of groundwater and the movement of water in the study area.

It was found that the groundwater and the surface water at PPC Mooiplaas is mainly characterised by Ca^{2+}-Mg^{2+}-HCO_3^- type of water. The groundwater is mainly freshly recharged groundwater with lower average values of pH than the surface water. When the inorganic chemistry results of PPC Mooiplaas was compared to the surrounding karts aquifer chemistry it was seen that the mine has high amounts of NO_3^- in it. It was also seen that the Hennops River is contaminated by sewage due to the high concentrations of NH_4^+

and very small amounts of NO_3^-. This indicates that the NO_3^- contamination caused by PPC Mooiplaas has a very small impact on the river but it still has a substantial impact on the groundwater downgradient of the mine. The hydrogeochemical at PPC Mooiplaas is consistent with the understanding of what groundwater in a karst environment is. The study also showed that mining dolomite at PPC Mooiplaas does not have detrimental environmental effects besides elevated NO_3^-.

In addition to assessing the hydrogeochemistry of the water samples collected at PPC Mooiplaas stable isotopes were used to identify the source and possible pathways of the water in the study area. The isotope data indicated that the WPS water is freshly recharged groundwater with the Expl BHs possibly being the source of water seeping at the WPS. The isotope data also showed that the wall leaks, WPWS and EPWS both have a component of SsD since both these sampling locations deviate from the LMWL. The major surface water bodies e.g. the WP, EP and the FD is groundwater with a slight evaporation signature.

PPC Mooiplaas is a great example of the effects a dolomite mine has on a karst aquifer with the main impact being an increase in NO_3^- concentration. High amounts of NO_3^- can cause serious negative effects to human health if consumed therefore, it is recommended that the PPC Mooiplaas treats the water for NO_3^-. PPC Mooiplaas would be ideal to conduct further studies at like such as tracer test along the dykes and faults which will be valuable to understand movement of contamination in a karst aquifer. It is possible that the NO_3^- contamination is isolated within the compartment since these compartments are known to be barriers. It is recommended that NO_3^- is used as a tracer to investigate if water and its contaminants move across these boundaries. A hydrocensus was not included in this study. It is recommended the a thorough hydrocensus is conducted with the main objective to obtain groundwater level data in the surrounding area. This will enable a better understanding of the groundwater flow direction in the study area.

Declaration

I, Christel van Staden declare that the thesis/dissertation, which I hereby submit for the degree MSc Hydrogeology at the University of Pretoria is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

Signature

Date

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Abbreviations

AMD	Acid Mine Drainage
CGS	Council for Geoscience (Est 1993 formerly the Geological Survey of South Africa)
DD	Decimal degrees
DME	Department of Minerals and Energy
EC	Electric Conductivity
EP	East Pit
EPWS	East Pit Wall Seep
Expl BH N	Exploration Borehole North
Expl BH S	Exploration Borehole South
FD	Fish Dam
GCS	Groundwater Consulting Services
GMWL	Global Meteoric Water Line
GWF	Groundwater Flow
HRDS	Hennops River Downstream
HRUS	Hennops River Upstream
ICP-OES	Inductive Coupled Plasma-Optical Emission Spectroscopy
km	Kilometre
LMWL	Local Meteoric Water Line
m	Meter
mamsl	Meters above mean sea level
max	Maximum
mbgl	Meters below ground level
MDV SyD	Metallurgical Dolomite Crusher ("Vergryser") Slurry Dam
min	Minimum
ML	Megalitre
N/W	North West
N/E	North East
n	Number of samples
PI	Plant Inlet
PPC	Pretoria Portland Cement

PMWL	Pretoria Meteoric Water Line
PWC	Price Waterhouse Coopers
RPD	Relative Percent Difference
SD	Standard Deviation
SsD	Slimes Dam
SyD	Slurry Dam
TDS	Total Dissolved Solids
TH	Total Hardness
US	United States
UK	United Kingdom
WP	West Pit
WGS84	Since 1 January 1999, the official co-ordinate system for South Africa is based on the World Geodetic System 1984 ellipsoid, commonly known as WGS84, with the ITRF91 (epoch 1994.0) co-ordinates of the Hartebeesthoek Radio Astronomy Telescope used as the origin of this system. This new system is known as the Hartebeesthoek94 Datum.
WPS	West Pit Seep
WPWS	West Pit Wall Seep

1. Introduction

Dolomite has a multitude of uses in almost all countries globally and it is also found in economically viable quantities in most countries. There are three principal industries dolomite are used in, and these are: cement manufacturing, metallurgical processes and agriculture. In South Africa, there are approximately 43 quarries where dolomite is mined and the main drivers in South Africa for dolomite are the uranium and gold industries; the cement industry and to a much smaller extent the agricultural industry (DME, 2003). One commodity related to dolomite, but not necessarily to the mining of dolomite, are karst aquifers that form in dolomite terrain. Karst aquifers are formed by the dissolution of dolomite rock; a process called karstification. Karstification is a vital process in dolomite because it leads to the formation of high yielding aquifers, which are an essential source of water in South Africa (Buttrick et al., 1993). Boreholes in dolomite, where karstification has taken place, are usually high yielding due to highly permeable zones that have high storage capacity (Leyland, 2008). Due to the large storage capacity and good quality of karst aquifer these systems are major freshwater resources for domestic, industrial and agricultural uses and also one of the most important resources for drinking water worldwide (Dişli, 2019). One example of such an aquifer in South Africa is the Fountains East and Fountains West Springs located in the Groenkloof Nature Reserve, in the City of Tshwane. These springs have been supplying communities with water since 1855 and the only treatment is chlorination (Haaroff et al., 2012).

Karst aquifers are known to be highly susceptible to contamination since pollutants can travel far distances in a very short amount of time. Due to the high vulnerability of karst aquifers, understanding the hydrogeochemical properties of these aquifers are highly significant for the management, protection and sustainable development.

The aim of this study is to understand the impact PPC Mooiplaas has on the karst aquifer it is mining into since, karst aquifers are highly vulnerable to pollution (Leyland, 2008) Therefore studying the anthropogenic influences on it will help one to understand and prevent damage to the aquifer. Understanding the influence of mining on a karst aquifer is important since water is the most important resource on earth and this fact has become abundantly clear in the past several years as drought has been experienced severely in several parts of South Africa.

1.1. Objectives

There are five main objectives of this study: The first is to characterise the hydrogeochemistry of the PPC Mooiplaas and the second is to compare the water quality of PPC Mooiplaas to that of it surrounding karst aquifer. The third is to identify the movement of water within the study area by stable isotope analysis and the fourth is to identify the source of water within the study area. Then lastly it is to understand how the anthropogenic activity impacts the karst aquifer. The best place to conduct a study like this is at the Pretoria Portland Cement Mooiplaas dolomite mine (PPC Mooiplaas) near Laudium, Gauteng. The reason being that the mine is interfering with the karst aquifer and PPC Mooiplaas is ideal due to the multiple anthropogenic influences occurring at the mine and in its surrounding area. Therefore, conducting a hydrogeochemical assessment at PPC Mooiplaas will help understand how anthropogenic activity influences a karst aquifer and to do a hydrogeochemical characterisation of a karst aquifer. The different water components that interact with each other will also aid in understanding the movement of the water in the study area.

To achieve the objective the different components of water at PPC Mooiplaas will be sampled and tested for chemistry and stable isotopes. By doing this a better understanding and characterisation of the different components of water that interact with each other in the study area will be gained. By understanding and characterising the different water components in the study area the influence of anthropogenic activity on a karst aquifer will become clear. Understanding the anthropogenic influences on a karst aquifer is important since water is the most important and valuable resource on the earth and this fact has become abundantly clear in the past several years as drought has been experienced severely in several parts of South Africa.

1.2. Dolomite in South Africa

Dolomite is a common rock formation in South Africa. It covers approximately 25% of the Gauteng province, with parts also encountered in the Northern Cape, Mpumalanga, North West and Limpopo provinces. These dolomite formations are from the late Archean to early Proterozoic rocks of the Transvaal and Griqualand-West Supergroups and are distributed in the Kaapvaal Craton in the Transvaal Basin and the Ghaap and Prieska Subbasins in South Africa. The chemical sedimentary rocks of the Transvaal and Griqualand-West Supergroups are the Chuniespoort and Ghaap Groups respectively (**Figure 1**). The Chuniespoort and Ghaap Groups have been researched in detail by Altermann and Wotherspoon (1995), Eriksson et al. (2006), and several others.

The formations of relevance in this study are within the Chuniespoort Group, known as The Karst Belt that stretches from Delmas and Springs in Gauteng to the border of Botswana, with a length of 300 km (**Figure 1**) (Oosthuizen & Richardson, 2011). The limestone and dolomite within the Chuniespoort Group are in the Malmani Subgroup with the Penge Formation, which is iron formations, overlying the Malmani Subgroup. The Chuniespoort Group originally formed through chemical and organic precipitation of calcium and magnesium carbonates, which left stromatolite structures in the rock formations. According to Brink (1979), limestone was the original deposit, which was replaced through dolomitization by dolomite and chert as a secondary replacement rock. The karstic aquifer within the Malmani Subgroup contain a lot of water and decanting of this water usually took place over dykes or the adjacent Witwatersrand Supergroup that causes a boundary and is the reason that several fountains developed. All these fountains are also the reason that many farms' names in the Central and West Rand contain the word "fontein", meaning "fountain" for example, Vogelfontein, Elandsfontein, Driefontein etc. (Durand, 2012).

1.2.1. Karst aquifers

A common process that occurs within the Malmani Subgroup is karstification, which is the result of weathering processes. Rainwater that mixes with carbon dioxide (CO_2) in the atmosphere and soil, forms a weak acidic groundwater that moves along fractures within the dolomite, resulting in the dissolution of the dolomite and causing karstification. This chemical process can be represented by **Equation 1**.

$$\boldsymbol{Dolomite: CaMg(CO_3)_2 + 2H_2CO_3 \rightarrow Ca(HCO_3)_2 + Mg(HCO_3)_2} \quad \textbf{\textit{Eq. 1}}$$

Karstification is dependent on several factors, which include quantity of precipitation, partial pressure of CO_2 and hydraulic gradient. Climate is a large factor, since it controls CO_2 concentration as well as temperature (Holland, 2007). One of dolomite's characteristics are that it is impermeable. Therefore, another factor that karstification relies on is structural features like faults, dykes, fractures and bedding planes, because it allows water to move through the dolomite to the water table, which enables karstification.

Karstification causes dolomite to develop high permeability zones and sometimes voids that have very high storage capacity that permits the rapid transport of groundwater. Karst aquifers usually have high yielding boreholes and springs with good quality groundwater. Although these karst aquifers are a major water commodity, the sinkholes or surface subsidence that occur in dolomitic terrain in Gauteng have been a cause of major concern for many.

1.2.2. Sinkholes and surface subsidence

A sinkhole occurs when the ground surface suddenly collapses which can lead to death, injury and structural damage. Surface subsidence is a depression that forms due to compression at a depth of low-density dolomite material. Sinkholes and surface subsidence are both prone to occur in areas underlain by dolomite rock and due to an increase in urbanisation of Gauteng. Here sinkholes have become a prominent risk. Sinkhole development is exponentially more common in urban areas than in undeveloped areas (Meyer, 2014).

There are two mechanisms that result in the formation of sinkholes and surface subsidence, namely ingression or dewatering. Ingression occurs when leaking water or a concentrated ingress of water causes subsurface erosion. The erosion results in the downwards transportation of material to cavities deeper underground and as a result in time an arch will form that will cause a sudden collapse. The second mechanism is dewatering which occurs when the groundwater level is lowered, resulting in an increase in erosion also transporting material downward to cavities deeper underground leading to a sudden collapse (Oosthuizen & Richardson, 2011).

Sinkholes can occur with very little warning and can form holes in the ground up to 125 m in diameter with steep sides and depths of up to 50 m (Oosthuizen & Richardson, 2011). Sinkholes have cost the City of Tshwane R118 million on preventative and remedial dolomite projects in the 2017/2018 financial year (BusinessTech, 2018). Sinkholes do not only have a financial implication but according to Buttrick et al. (2001) sinkholes have also caused 38 people’s deaths in the 50 years prior to 2001 in South Africa.

Even though sinkholes are a naturally occurring process it is due to leaking water infrastructure, poorly managed surface water drainage and groundwater level drawdown that approximately 98% of the sinkholes occur in densely populated or mining environments (Oosthuizen & Richardson, 2011).

1.3. Contamination, mining and dolomite

The dolomite mining industry is not the only mining industry that influences the aquifers in The Karst Belt. The gold mining industry also has a major impact on the karst aquifers. The world's largest gold deposit was discovered in the Witwatersrand Supergroup, adjacent to the Malmani Subgroup and resulted in the founding of Johannesburg in 1886. Mining of gold in the Witwatersrand Supergroup is still continuing today and with better technology mining operations have been able to continue deeper into the earth. With the increasing depth of the gold mines, water inflow from the dolomite rocks became a huge problem for the mines, and continuous dewatering was required to allow for mining activity to continue. The continuous dewatering of the mines led to springs in the dolomite drying up (Dreybrodt, 1996) and also led to surface subsidence (Kleywegt and Pike, 1982). The dewatering of the mines is not the only negative impact the gold mining industry had on the karst aquifers in the Malmani Subgroup, as contamination due to acid mine drainage (AMD) also poses a massive problem (Durand, 2012).

Although gold mining is only one cause of contamination and sinkholes within the dolomites, it is not the only concern. A lot of informal settlements have been established in and around the Tshwane metropolitan like Atteridgeville, Tembisa and Soweto. These informal settlements usually have poor to no infrastructure for sewage and wastewater leading them to use natural streams and rivers as drainage systems for waste and sewage, which in turn leads to a major source of contamination of the karst aquifer system.

1.3.1. Different types of mining methods

The type of mining method used, depends on the type, size and location of the ore body. There are two main categories of mining methods, namely underground mining and surface mining. Underground mining is any type of mining where the miner or any machinery works underneath a roof of rock. Types of underground mining include methods like room-and-pillar mining, vein mining, longwall mining, block caving and several more. These mining methods are complicated and are usually designed to fit the needs of extracting the ore body (Hamrin, 2001). The most economic mining method and the method that accounts for more than 80% of mineral extraction since 1990 is open cast mining. Ore bodies close to the surface mainly include coal, evaporite deposits and road quarry material. Surface mining methods include strip mining, open pit mining, dredge mining, placer mining and hydraulic mining in riverbeds, terraces and beaches (Ochieng et al., 2010). Surface mining is the main topic of this report and will therefore be discussed in further detail.

There are several ways surface mining is implemented, however there are three main steps every mine follow. The first step is the stripping of the non-economic overburden material, secondly it is the mining of the ore and then lastly the restoration and rehabilitation. The type of surface mining is determined by how the three steps are executed. Open-pit mining is when the overburden is excavated and removed from the pit and stored somewhere else, then the ore is extracted by horizontal benches. The benches can be between 18-45 m wide, 9-30 m high and can have a slope of between 50°-70°(Prokop et al., 2004). After the ore is extracted, the pits are mostly left open and pit lakes develop since the groundwater is no longer being pumped away. The term quarry has different meanings in different countries. In the United Kingdom (UK), the word quarry refers to any non-coal surface mine whereas in the United States (US) it means a surface mine that produces dimension stone. For the purposes of this study, the UK meaning will be used. Open cast mining or strip mining is like open-pit mining but the one main difference is that the overburden is cast into an old mined out panel and not excavated and deposited somewhere else (Prokop et al., 2004).

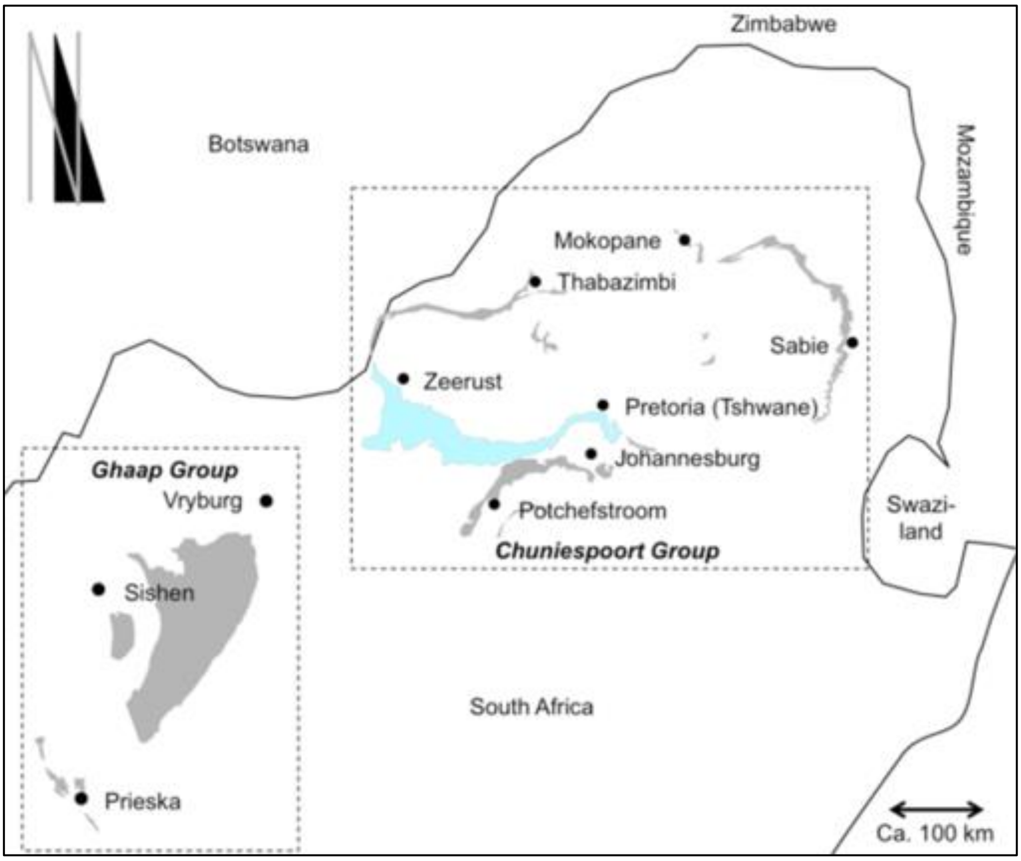


Figure 1: The occurrence of dolomite rock in South Africa and The Karst Belt indicated in blue (Adapted from Dippenaar et al., 2018).

1.3.2. Mining and mine water

The South African mining sector is an important industry for industrial and economic growth. The mining industry is responsible for approximately 5% of direct employment and for each direct job another two indirect jobs are created (Price Waterhouse Coopers, 2017). In contrast to the favourable economic effect, the mining industry has adverse effects on the surrounding environment. With the increasing financial pressure and downsizing of the mining industry, emphasis is placed on open cast mining because it is a faster and more economical way of extraction with a higher percentage of recovery compared to underground mining. However, opencast mining is more damaging towards the environment than underground mining. Open cast mining disturbs the natural ecosystem, but also generates its own artificial system that includes contaminants and has a negative effect on the surrounding environment (Mishra et al., 2004).

When surface mines are being excavated, it removes portions of the aquifer. This results in loss of a water resource medium and water itself due to an increase in evaporation.

The removal of the overburden above the aquifer also causes an increase in vulnerability to the aquifer due to the removal of the protecting barrier (Prokop et al., 2004). These are merely the obvious impacts of surface mining on groundwater, but there are several more.

The sides of a surface mine develop a "halo" of high permeability due to blasting and a reduction of lateral stress. The high permeability in the pit walls can cause turbulent flow near the pit, resulting in a steep water table compared to the natural water table (Dudgeon, 1985). Another effect on the groundwater level around the pit is that the water level tends to be a steeper up-gradient of the pit and a much gentler down-gradient of the pit (Morgan-Jones et al., 1984). This alters the hydrogeology of the area completely. Pit lakes can form and are usually in continuity with the surrounding groundwater, but there are cases where the floor of the pit lake is covered with fine sediment, causing the pit lake to be perched from the groundwater and minimizing the interaction of the pit lake with the groundwater (Prokop et al., 2004).

From a limnological and geochemical perspective, pit lakes are complex environments. The key difference between a pit lake and a natural lake is the relative depth (D_R) (Castro & Moore, 2000).

$$\boldsymbol{D_R = 100\left(\frac{Z_m}{d}\right)} \qquad \textbf{\textit{Eq. 2}}$$

- Zm is maximum depth of a water body
- d is the standard diameter

The D_R calculation is shown in **Equation 2.** The D_R of a natural lake is usually less than 2% and it can rarely reach a maximum of 5%, whereas a pit lake has a D_R between 10%-40%. The consequences of such high D_R values are limited evaporation losses as a percentage of the stored water body. The limited evaporation loss causes a density stratification in the pit lake that will promote a three-layer system where the deepest layer is not involved in seasonal turnover. Such conditions are called meromictic conditions (Bowell, 2002).

As seen in **Figure 2** the earth's surface is a reaction front between the oxidising, acidic atmosphere and the reducing, basic geosphere. Water is the medium that carries atmospheric reactants like oxygen and carbon dioxide into the geosphere. The zone where circulation of groundwater occurs between the atmosphere and the geosphere can mainly be characterised by redox and acid-base reactions. The rate of these reactions is increased around mining activities because they allow for rapid circulation of the atmosphere through the geosphere material that has been removed from its natural place and put in waste dumps (Prokop et al., 2004).

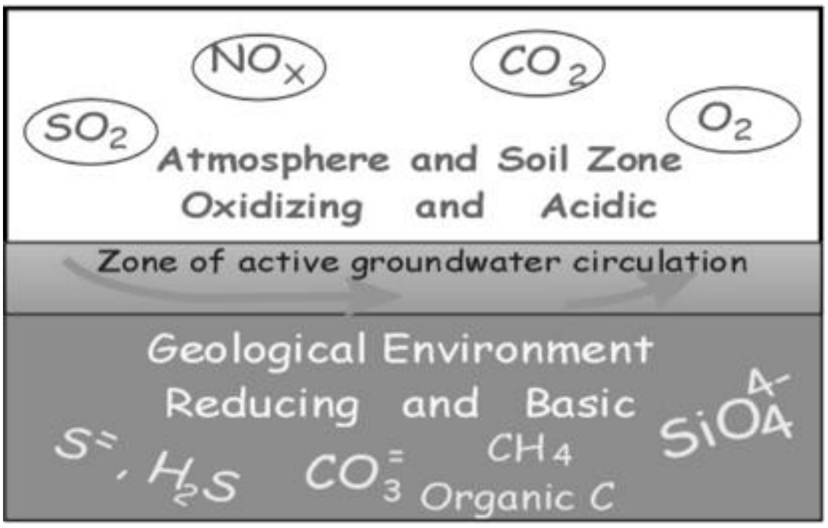


Figure 2: Reaction between atmosphere and geosphere (Prokop et al., 2004).

1.3.3. Geochemistry of mine water

Groundwater is water that is present beneath the surface of the earth. With that definition in mind, mine water is a type of groundwater that is subject to the same geochemical processes as normal groundwater when it percolates into the ground. There are several processes that govern the geochemical signature of a groundwater body (Prokop et al., 2004).

The first is recharge chemistry, which is determined by the fresh rainwater or snowmelt that recharges the groundwater. The newly recharged water may have similar isotopic (^2H, ^3H, ^{18}O), chloride (Cl^-) or pollutant (nitrates or sulphate) characteristics of the rainwater in the same geographical location (Banks et al., 1998). The soil zone has a large influence on the chemical characteristics of the groundwater, because recharge water moves through the soil zone before it can recharge the groundwater. The soil usually has a high content of microbes, resulting in respiration, which increases the CO_2 content of the water before it recharges the groundwater. The third variable is the mixing of different water bodies (Prokop et al., 2004). Water-rock interaction is the fourth geochemical process that governs the chemical signature of groundwater. There are a multitude of different rock types, with many different mineral combinations that can alter the chemistry of the water, but generally in natural circumstances, O_2 and CO_2 are consumed, the pH gets elevated and there is the production of alkalinity. The production of alkalinity results in groundwater having a neutral to slightly alkaline pH. The reactions that take place between water and rock can be divided into four main categories:

Dissolution reactions

Dissolution reactions happens when a substance forms a solution in a solvent, and for water-rock reactions, water is the solvent and the rock dissolves into the water. An example of a dissolution reaction is the dissolution of calcite and can be represented by **Equation 3**.

$$\boldsymbol{Calcite: CaCO_3 \leftrightarrow \ Ca^{++} + CO_3^{2-}} \qquad \textbf{\textit{Eq. 3}}$$

Ion exchange reactions

This is a chemical reaction between two substances where ions of equal charge interchange. This type of reaction often takes place on the surface of clay minerals as seen for a Ca-clay and can be represented by **Equation 4**.

$$\boldsymbol{Ca - clay + 2Na^+ \leftrightarrow Na_2 - clay + Ca^{2+}} \qquad \textbf{\textit{Eq. 4}}$$

Acid-base reactions

This type of reaction is characterised by the consumption of CO_2, elevation of pH, release of bicarbonate alkalinity and the release of base cations. The most common rock forming minerals like carbonates and silicates result in the consumption of protons, as seen in **Equations 5 and 6**.

$$\boldsymbol{Calcite: CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-} \qquad \textbf{\textit{Eq. 5}}$$

$$\boldsymbol{Plagioclase: 2NaAlSi_3O_8 + 2CO_2 + 3H_2O \leftrightarrow 2Na^+ + 2HCO_3^- + Al_2Si_2O_5(OH)_4 + 4SiO_2} \qquad \textbf{\textit{Eq. 6}}$$

In normal groundwater, these types of reactions dominate, resulting in a neutral to slightly alkaline pH with base cations (Ca^{++}, Mg^{++}, Na^+) and bicarbonates.

Redox reactions

Redox reactions are chemical reactions where the reactions cause changes to the oxidation states. There are two types of redox reactions: oxidation and reduction. Oxidation reactions often release acid whereas reduction reactions often consume acid and release alkalinity. The redox reaction of nitrogen by organic matter is well documented and plays an important role in aquifers (Appelo and Postma, 2005) and can be represented by **Equation 7**.

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + H_2CO_3 + 2H_2O \qquad \textit{Eq. 7}$$

These different types of reactions result in distinct chemical changes to water, which enables someone to use the chemical differences to understand where the water came from and how it has been altered. The chemistry of groundwater is a valuable source of information that can be utilised to understand the movement of water within a study area.

1.3.4. Groundwater chemistry of a dolomite mine

Two case studies by Mishra et al. (2004), and Saliu and Shebu (2012) was found which discussed the environmental contaminants of mining a calcite, limestone and dolomite. The study by Mishra et al. (2002) is located in Biramitrapur, India and the study by Saliu and Shebu (2012) is located in Ikpeshi, Nigeria. Both the studies sampled water at several locations on the mines and compared the chemistry results to tolerance limits for drinking water standards of the respective countries. The study from Mishra et al. (2004) found that water from the mine had elevated total hardness, Ca^{2+} and Mg^{2+} of approximately 300 mg/L, 80 mg/L and 60 mg/L respectively. The study also reported small amounts of several other parameters, but none raised concern. The study from Saliu and Shebu (2012) also reports good quality water with hardness only elevated to >300 mg/L and chloride elevated to more than 300 mg/L.

1.3.5. Mine water as an environmental resource

From Mishra et al. (2004) and Saliu and Shebu (2012) it is clear that the water from a calcite, limestone and dolomite mine generally have good quality groundwater with minor elevated parameters. This is in contrast to general mine water, which is considered as a negative thing that is unremittable, but in reality mine water can also be regarded as an environmental resource (Banks et al., 1996). Some examples are:

- Mine water is usually bacteriologically pure and can be used as base flow to rivers that are heavily contaminated with sewage.

- Some limestone mines have such high-quality water that it can be used as drinking water.
- Mine waters can be a source of minerals like alkali salts or barium.
- Ferruginous mines' water is a recognised flocculent and can be used at sewage plants.
- Mine water can sometimes be used as a base heat pump solution for space-heating and the cooling of buildings.

1.4. Groundwater chemistry

The chemical signature of the different waterbodies will be used in this study to understand the movement of water in the system. This approach was chosen because it has a wide variety of uses in understanding the hydrogeology of an area, which include: quantitative and qualitative estimates of recharge, identification of the source of recharge, velocities and travel times of water movement, assessment of preferential flow paths and more (Scanlon et al., 2002 and Healy, 2010).

1.4.1. Master variable: pH

pH is a measure of the hydronium ions (hydrogen protons) in a solution and can be described as seen in **Equation 8**.

$$\boldsymbol{pH = -log_{10}[H^+]} \qquad \textbf{\textit{Eq. 8}}$$

A pH of 7 means that the activity of the hydrogen ions is equal to 10^{-7} mole/L or 0.0001 mg/L. pH is considered a master variable because it controls the hydrochemistry of a sample. The concentrations of dissolved carbon species depend on the pH of a solution and this concept is visually presented in **Figure 3**. At pH levels between 0 to 6.3 the H_2CO_3 species will be more prominent. With pH values between 6.3 to 10.3 the HCO_3^- species will be even more prominent and then with a pH above 10.3, CO_3^{2-} will be most prominent.

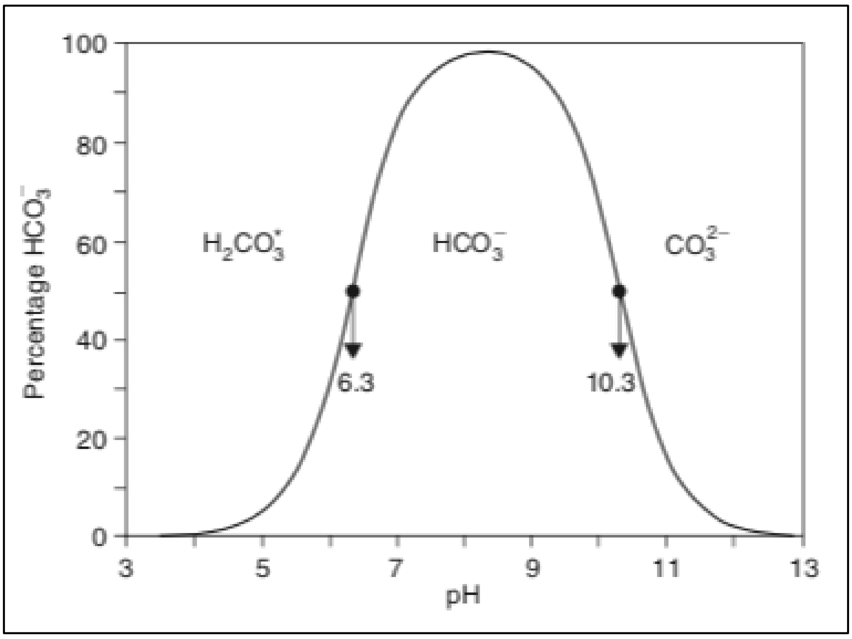
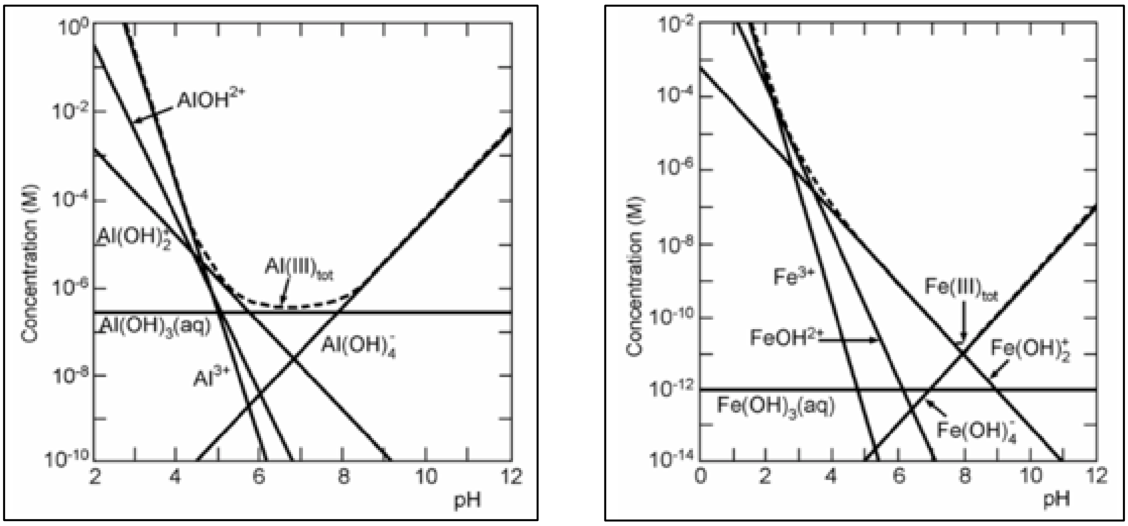


Figure 3: Percentage of dissolved carbonate as a function of pH (Appelo & Postma 2005).

Similar to carbonate species, the water-rock reactions and the solubility of metal ions like aluminium, iron and zinc also depend on the pH of a solution. **Figure 4** is two diagrams depicting the concentration of aluminium- and iron-hydroxide vs. pH. The solid lines show the concentration of specific ions at a specific pH and the dashed line shows the total solubility of the ions in water. Aluminium is highly insoluble in water with a pH between 5-8, but in water with an acidic and alkaline pH, the solubility of aluminium starts to increase. In contrast to aluminium, ferric iron is particularly insoluble at pH values greater than 3-4.



(a) (b)

Figure 4:(a) Solubility of aluminium hydroxide and its pH dependence (b) solubility of iron hydroxide and its pH dependence (Younger et al., 2002).

1.4.2. Chloride and bromide ions

Chloride (Cl^-) and bromide (Br^-) are halides and both have similar chemical characteristics. For example, Cl^- and Br^- have the same charge, do not participate in redox reactions, are non-reactive, are not adsorbed onto organic or mineral surfaces and do not form insoluble precipitates. Due to these chemical characteristics both these ions are used as tracers in groundwater studies because the ions are conservative (non-reactive) and the ions do not form insoluble precipitates (Fetter, 1993). All these properties make them good tracers in a hydrological study.

The Cl^- ion occurs in several anthropogenic sources. As an example, Cl^- occurs in sources like industrial discharge, sewage, animal waste, fertilizers and several others. Due to these anthropogenic sources of Cl^-, the Cl^- ions can be used to trace and understand the movement of water (Scanlon et al., 2002).

There are several studies that use Cl^- and Br^- as tracers to understand the hydrogeology of the vadose zone. Pronk et al. (2009) monitored rainfall events and used several parameters, including Cl^- and Br^-, to understand the function of the vadose zone. By understanding the chemical signature of a specific rainfall event, Pronk et al. (2009) could characterise the flow of water in the vadose zone of karst terrain.

In this study, the anthropogenic influence on water chemistry will be used to understand the movement of water through the study area.

1.4.3. Groundwater chemistry in karst or dolomite

Groundwater chemistry of karst aquifers is mainly controlled by the weathering of carbonate minerals such as calcite and dolomite as well as evaporative minerals like gypsum and halite. The groundwater chemistry of karst aquifers is also controlled by rainwater and surface water interaction and anthropogenic activity (Dişli, 2019; Appelo and Postma, 2005). Several studies indicate that the typical groundwater type for karst aquifers is Ca^{2+}-Mg^{2+}-HCO_3 (Dişli, 2019; Gu et al., 2017; Yuan et al., 2017; Williams, 2007). A useful way to display lots of the chemistry data of water, is on a Piper diagram which also allows one to see the water type. A Piper diagram makes use of two triangular charts which allows the depiction of cation and anion proportions, and the water type is then depicted at the place where the data is plotted on the central diamond. **Figure 5** is an example of a Piper plot depicting different fields that result from plotting the chemistry data of bottled mineral water that is abstracted from different rock types. From **Figure 5** one can see Ca^{2+}-Mg^{2+}-HCO_3 type water plots in the left corner of the diamond that is also seen in several studies done on karst or dolomite groundwater (Dişli, 2019; Gu et al., 2017).

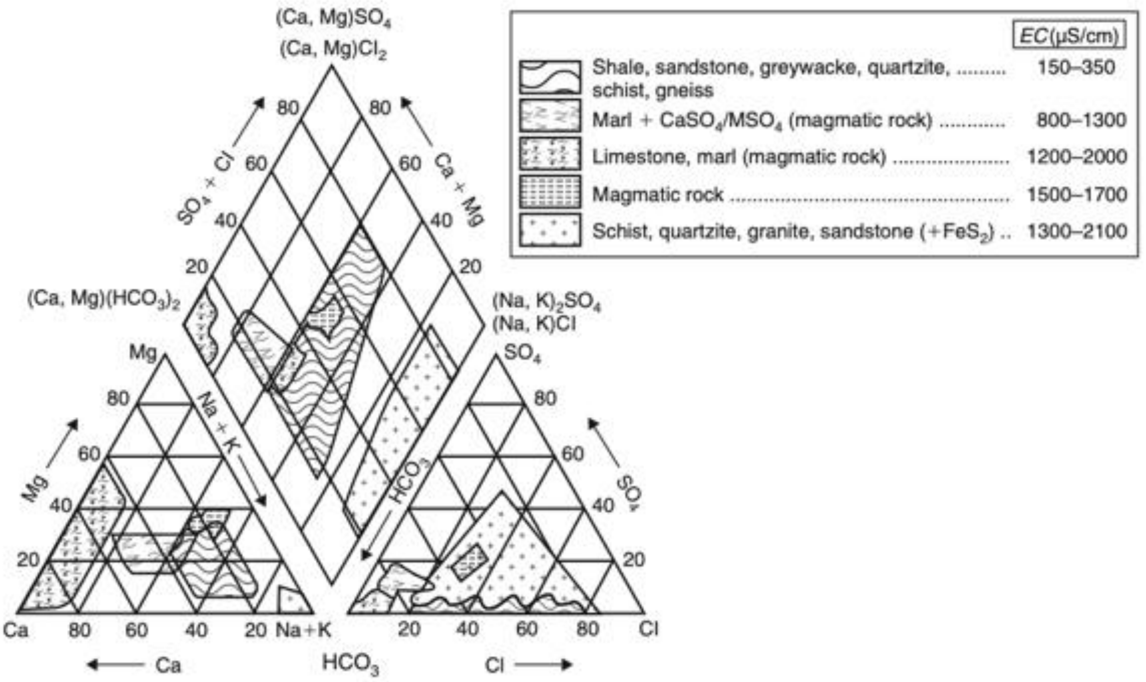


Figure 5: Piper plot of bottled mineral waters originating from different rock types (Appelo and Postma, 2005).

A Ca^{2+}-Mg^{2+}-HCO_3^- water type of water that is found in karst or dolomite aquifers around the world is consistent with what is found in karst in South Africa (Meyer, 2014 and Holland & Witthüser, 2008; Hobbs and Cobbing, 2007; Mndaweni et al., 2019). Meyer (2014) further indicate that in some cases there are a distinct trend from Ca^{2+}-Mg^{2+} to Na^+-K^+ and from HCO_3^- to SO_4^{2-} or Cl^-. The trend from Ca^{2+}-Mg^{2+} to Na^+-K^+ is attributed to the Karoo formation that consists of shale and sandstones, and the trend from HCO_3 to SO_4^{2-} or Cl^- is attributed to anthropogenic influences. Holland & Witthüser (2008) also indicated that water influenced by contamination result in a water type change from Ca^{2+}-Mg^{2+}-HCO_3^- to Mg^{2+}-Ca^{2+}-SO_4^{2-} or Na^+-SO_4^{2-}.

The general trend for the majority of groundwater karst or dolomite studies is to use groundwater chemistry and isotopes to understand the flow systems and identify contaminants in a study area. In some cases, isotope data is limited or unavailable and therefore, the study depends only on chemistry data to gain an understanding of the flow system and contaminants (e.g. Holland & Witthüser, 2008).

1.5. Stable isotopes

Isotopes are atoms of the same element with different numbers of neutrons yet the same number of protons and electrons. Due to the different number of neutrons, the same element will have different masses with slightly different chemical and physical characteristics. For example, hydrogen occurs in nature as a mixture of ^{1}H and ^{2}H while oxygen is found in nature with atomic masses of ^{18}O, ^{17}O and ^{16}O and for every two ^{18}O atoms in the ocean there are a thousand ^{16}O atoms. This ration of $^{18}O/^{16}O$ or $^{2}H/^{1}H$ in natural waters can vary for each body of water therefore, isotopes of oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) have become a valuable method in understanding hydrogeological processes (Appelo and Postma, 2005). Heavier and lighter isotopes naturally fractionate and result in different signatures that can be used to identify different water bodies that originate from different sources. In hydrogeology stable isotopes are reported as per mil (‰) deviation from a standard, using δ (delta) notation (**Equation 9**). R is the isotope ratio of the heavier over the lighter isotopes (e.g. $^{18}O/^{16}O$ or $^{2}H/^{1}H$). The δ value is a ratio of the heavier isotope element to the lighter isotope element and this ratio enables the comparison of isotope data.

$$\delta(‰) = \frac{R_{Sample} - R_{Standard}}{R_{Standard}} \times \mathbf{10} \qquad \textit{Eq. 9}$$

1.5.1. Stable isotopes in rainwater

The main factors that cause variations in isotope ratios are evaporation and precipitation that result in fractionation. However, there are several other factors such as seasonal changes, latitude, longitude, altitude, melting, crystallisation and the rainfall amount that also have substantial effects on the isotope ratios (Pang et al., 2017). During evaporation, the lighter molecule of water ($^{1}H^{1}H^{16}O$) is more volatile and will enter the gas phase more readily than the heavier water molecule. The opposite is true during precipitation: The heavier ($^{2}H^{1}H^{16}O$ or $^{1}H^{1}H^{18}O$) isotopes will condense first before the lighter molecule will condense out of the gas phase. Therefore, the water vapour from the ocean will be depleted in heavier isotopes and the initial precipitation that results would be enriched with heavier isotopes. This process will continue, and the more inland evaporation and precipitation occurs, the more negative the isotopic signatures will become (Coplen et al. 2000).

Groundwater is recharged to a large extent by precipitation, but precipitation is not the only source of recharge to groundwater. Precipitation sometimes end up in rivers, ponds or snowfall, and as a result are exposed to evaporation before it infiltrates the groundwater system. Therefore, the isotope composition of the infiltrated water could differ from the surrounding precipitation. If direct infiltration occurs in the area, the groundwater isotopic ratios will be similar to the surrounding precipitation isotope ratios as seen in **Figure 6** (Pang et al., 2017).

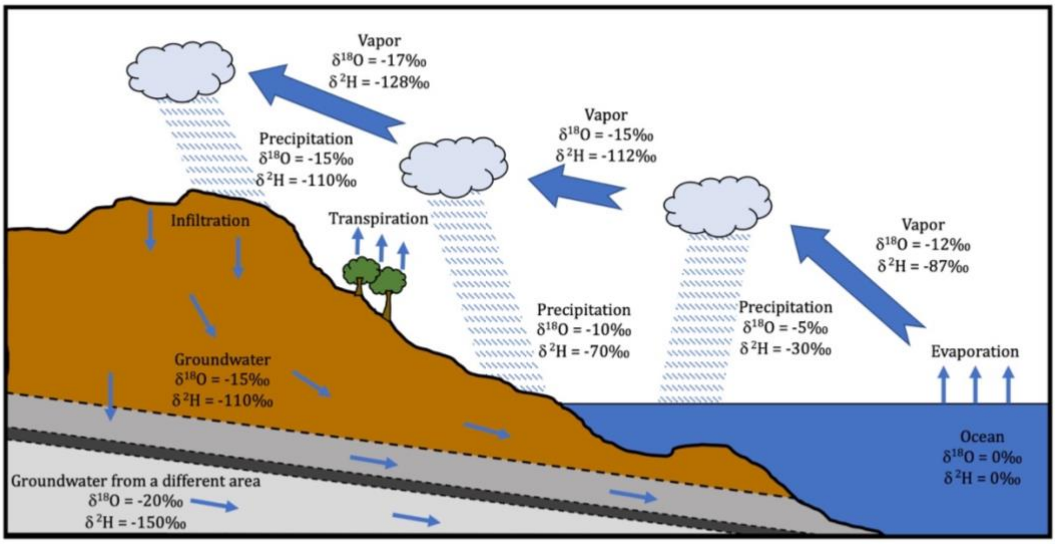


Figure 6: Stable isotope composition of the ocean, precipitation, vapour and groundwater. (adopted from Pang et al., 2017 and Coplen et al., 2000).

Due to the fractionation process the relationship between $^{18}O/^{16}O$ and $^{2}H/^{1}H$ generally yields a straight line. The relationship between $^{18}O/^{16}O$ and $^{2}H/^{1}H$ for worldwide precipitation samples can be represented by **Equation 10** and is known as the Global Meteoric Water Line (GMWL) (Craig, 1961). Localised isotopic ratios can be compared against the GMWL in order to understand the temperature controls of localised rainfall. However, the same but different relationship can be obtained for your local meteoric rainfall which is called the Local Meteoric Water Line (LMWL).

$$\boldsymbol{\delta^{2}H = 8 \cdot \delta^{18}O + 10} \qquad \textbf{\textit{Eq. 10}}$$

The LMWL is the best representation of the local isotopic water signature and it is a good baseline to compare other isotopic data to. Changes that deviate from the LMWL have been studied in depth by Pang et al. (2017) and general trend lines have been delineated as seen in **Figure 7** to illustrate isotope compositions that result from different processes. The evaporation line has a different slope which is usually smaller than that of the LMWL/GMWL and a mixture of e.g. precipitation and evaporated water would result in a perpendicular line between the LMWL and the Evaporated trend line (Eby, 2004). Different groundwater systems can also result in different water-rock reactions that result in H_2S, CO_2, silicate mineral and clay mineral exchange, which will also result in different trends for stable isotopes (Pang et al., 2017).

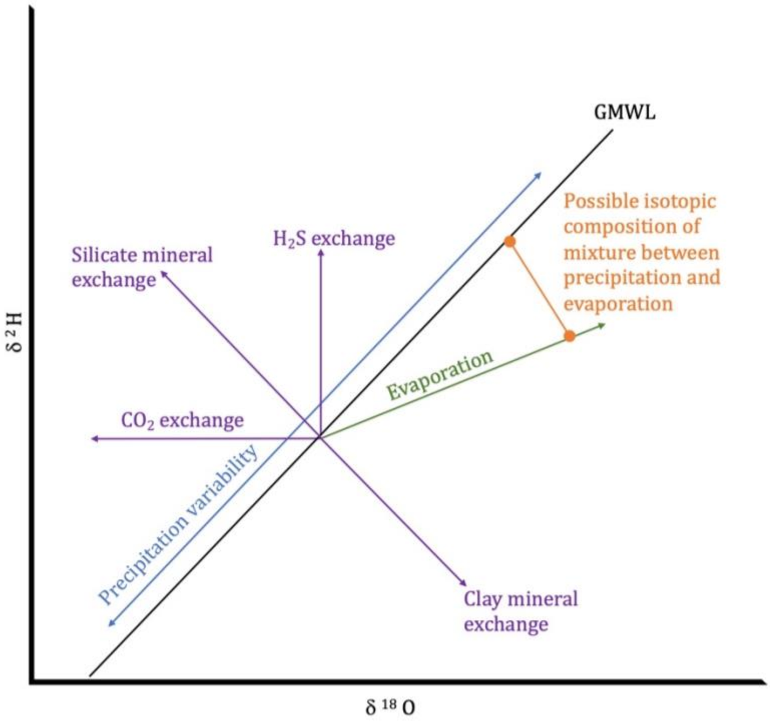


Figure 7: Different factors that cause variation in isotopic rations of stable isotopes (adopted from Pang et al., 2017 and Eby, 2004).

1.5.2. Stable isotopes in karst or dolomite

Globally, several studies have been done with isotopes in a karst or dolomitic environment. Isotopes were used to identify groundwater flow paths, connections between springs and sinkholes, quantifying flow velocity within karst aquifers and also groundwater recharge sources (Rusjan et al., 2019; Guo et al.,2019; Healy, 2010). However, with regards to isotopic studies within the Karst Belt of South Africa, only two studies were identified.

The first was a stable isotope study that was conducted in January 2009 for groundwater, the Maloney's Eye spring, surface water and rainfall collected during 2006 (Meyer, 2014).

The study area was located in the Steenkoppies and Zwartkrans Compartments which is west of Krugersdorp, Gauteng. The results of the δ^2H and δ^{18}O were shown relative to the Global Meteoric Line (GMWL) and also the Pretoria Meteoric Water Line (PMWL). The study found that the isotopic data of some groundwater samples correlated along an evaporation line indicating that the groundwater has been recharged by surface water. The study also found that the groundwater samples did plot along the PWML indicating quick local recharge events, which is typical for karst aquifers (Meyer, 2014).

The second was Naidoo (2014) which characterised the Fountains East and the Fountains West Springs Located in Pretoria, Gauteng with data obtained from Mr. Siep Talma and Dr. Eddie van Wyk. Part of the study was to characterise the water emanating from these springs with chemistry data and isotopic data. The isotopic data in the study found that the water emanating from the springs were recently recharged and that the likely source of the groundwater was rainfall. According to Naidoo (2014) the water from the springs is recharge by precipitation and the recharge zone is most likely outside of Pretoria, but that the source of the water for both the Fountains East and West Spring is the same.

2. Study area

The study area is the Pretoria Portland Cement Mooiplaas dolomite quarry (PPC Mooiplaas), seen in **Figure 8**, where metallurgical dolomite is mined in an open cast mine by means of bench-type mining. The mine was initially opened in 1956 by Iscor Limited and in 1969 PPC bought the Mooiplaas mine from Iscor (Page and Du Plessis, 1986). The main purpose of the mine was to produce metallurgical grade dolomite for steel plants in Pretoria, from the Lyttleton Formation in the Malmani Subgroup, Chuniespoort Group and Transvaal Supergroup. The criteria for metallurgical grade dolomite are low percentages of Al_2O_3 (<0.2%), K_2O (<0.2%), Na_2O (<0.2%) and SiO_2 (<3.5%) and these criteria are met by the lower portion of the Lyttleton Formation. The by-products of the mining for metallurgical dolomite are also used, resulting in four different products (Page and Du Plessis, 1986):

- metallurgical dolomite (chert poor)
- metallurgical dolomite powder (chert poor)
- aggregate (chert rich)
- agricultural lime (chert rich).

Figure 8: View of PPC Mooiplaas mine taken towards the west. The east pit is most clearly seen to the right of the picture and then the west pit seen just beyond the

east pit. The benches seen to the right are the northern face of the quarry; each bench is 10 m high. The initial crushing is done in the quarry with a small plant seen on the left of this picture where the dolomite is crushed and placed on a conveyer belt that transports the dolomite to the crushing plant that is to the north-east of this picture where further processing is done.

2.1. Location

PPC Mooiplaas is located near Laudium, Pretoria West, which is 15 km southwest of Pretoria, **(Figure 9)**. Laudium and Erasmia border the mine in the east, Atteridgeville in the north, Saulsville in the northwest and the Hennops River is less than 1 km from the southern boundary of the mine property. The total extent of the mining concession is 1 033 ha.

The mining concessions are part of the following farms (GCS, 2008):

- the remainder of Schurweplaas 353 JR (887 ha)
- Portion 64 and 15 of Mooiplaas 355 JR (21 ha and 134 ha respectively)
- Portion 8 of Erasmia 305 JR (1 ha).

The mining activity is only taking place in the eastern section of the property, which leaves a large area to the west that is less influenced by mining activity **(Figure 10)**.

2.2. Topography

The area is mainly on the southern slope of the Skurweberg ridge which has a typical east-west ridge pattern that copies the Pretoria topography. The altitude is approximately 1 400 m above mean sea level (mamsl). The underlying strata dip north, resulting in talus/scree slopes that occur on the southern side. Ravines occur on the northern and southern side of the Skurweberg ridge. The slope analysis subdivides the area into four groups (0 - 0.5 %, 5 – 15 %, 15 – 25 % and > 25 %) (GCS, 2008). The quarry is situated on the 0 – 15%, thus resulting in a low slope with a wide outcrop of the Lyttleton Formation (Page and Du Plessis, 1986).

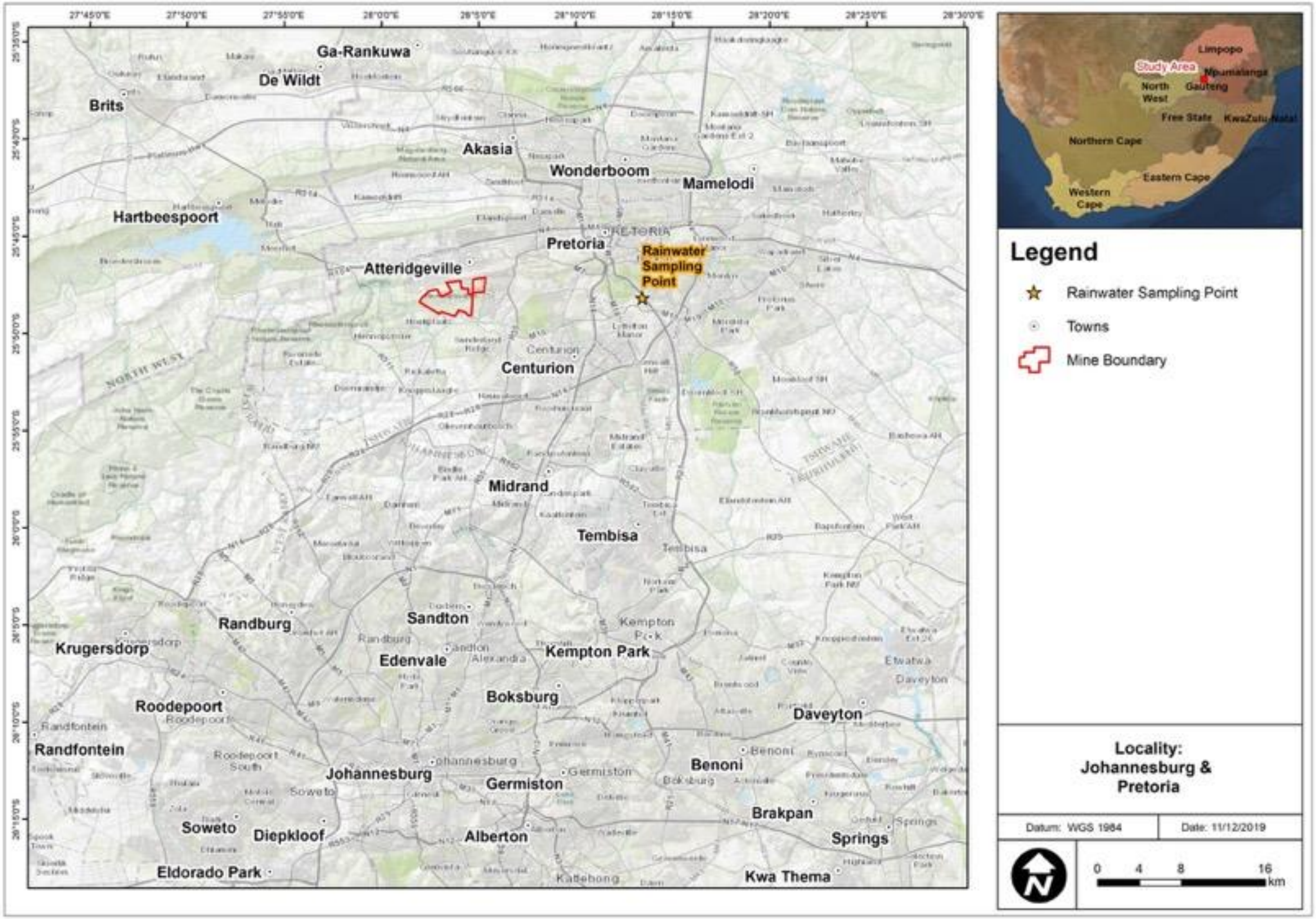


Figure 9: Location of PPC Mooiplaas within a regional setting on a 1:50 000 scale topocadastral map (2528CC).

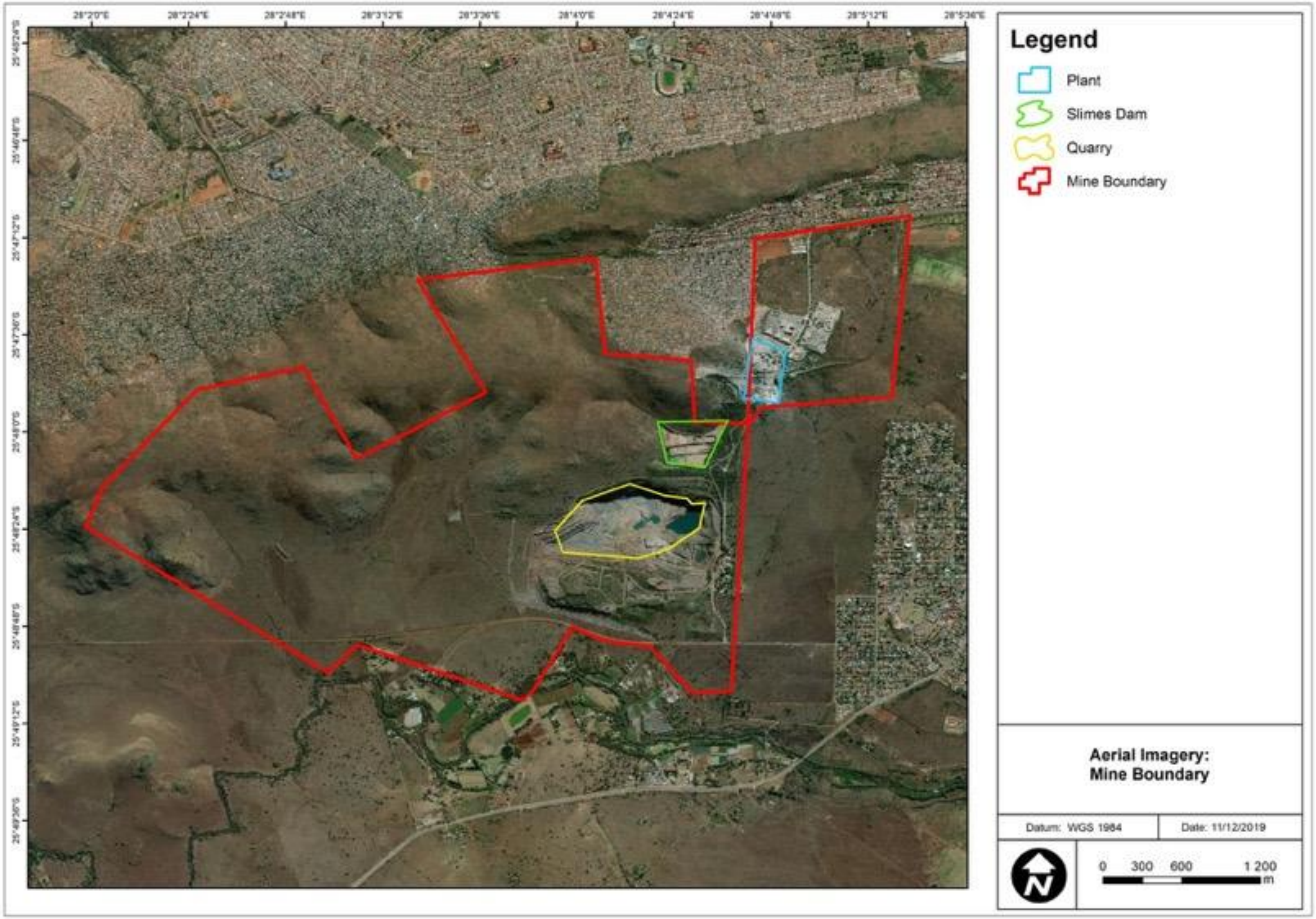


Figure 10: PPC Mooiplaas mine border, plant location, slimes dam location and quarry superimposed on an aerial photograph.

2.3. Climate

PPC Mooiplaas experiences a typical Highveld climate with cold dry winters and warm wet summers, during which 80% of the precipitation is derived from thunderstorms accompanied by hail. **Figure 11** shows the monthly average minimum and maximum air temperature distribution and **Figure 12** shows the monthly average rainfall and potential evaporation distribution for the PPC Mooiplaas area (Schulze, 2009). The long term (1950 – 2000) means annual precipitation for PPC Mooiplaas is 666 mm/a. From the rainfall and evaporation data it can be seen that the potential evaporation rates are far greater than the rainfall right through the year. The peak groundwater recharge period will be in the summer months when is highest.

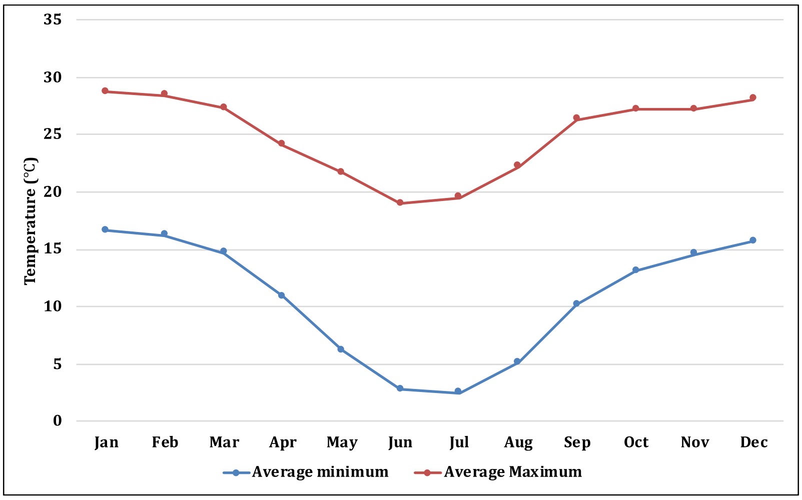


Figure 11: Monthly minimum and maximum average air temperature distribution for the PPC Mooiplaas area (Schulze, 2009).

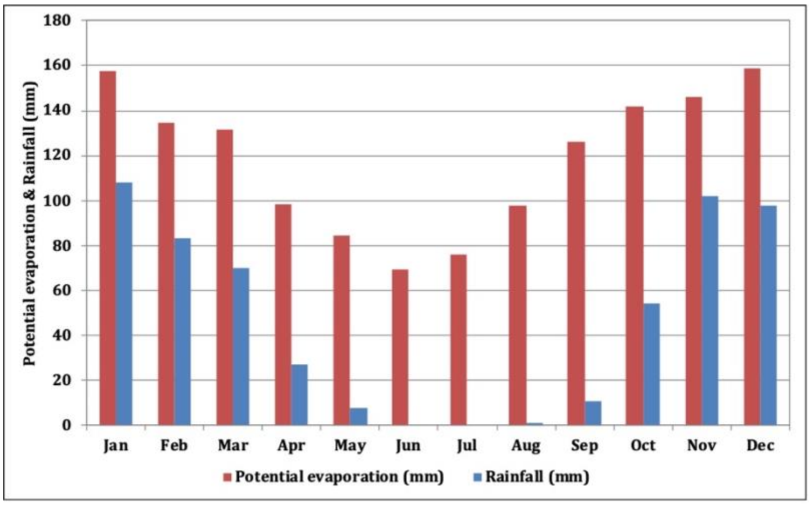


Figure 12: Monthly average rainfall and potential evaporation distribution for the PPC Mooiplaas area (Schulze, 2009).

2.4. Regional geology

The PPC Mooiplaas Mine is situated in the southwest region of Pretoria. This region consists of some of South Africa's oldest rock formations, like the Archean Halfway House granite. The Halfway House granite outcrops in a crescent-shape that stretches from the south of Centurion to central Johannesburg and from Krugersdorp to Kempton Park. The sedimentary rocks of the Transvaal Supergroup crop out just north of the Halfway House granite. The first formation, at the base of the Transvaal Supergroup, encountered just north of the Halfway House granite, is the Black Reef Formation that consists of quartzite, conglomerate and shale. The Black Reef Formation is followed by the chert interlayered dolomites of the Malmani Subgroup, and both the Black Reef Formation and the Malmani Subgroup make up the Chuniespoort Group (Eriksson et al., 2006). The Chuniespoort Group is overlain by the Pretoria Group, which consists of clastic sedimentary rocks like conglomerate, shale and quartzite. These geological units have been mapped by the Council for Geoscience on a 1:125 000 scale, as can be seen in **Figure 13,** with more detail presented in **Table 1**.

The Malmani Subgroup, the main interest in this study, can be traced all along the southern outcrops of the Transvaal Supergroup (SACS, 1980). There are five formations in the Malmani Subgroup, as seen in **Table 1**, but PPC Mooiplaas is mainly interested in the Lyttleton Formation, which is underlain by the chert-bearing Monte Cristo Formation and overlain by the chert-rich Eccles Formation.

Table 1: Stratigraphy of the study area (Meyer, 2014)

Code	Supergroup	Group	Formation	Description
Q	-	-	-	Alluvium
Vsi	Transvaal Supergroup	Pretoria Group	Silverton	Shale, carbonaceous in places; hornfels, chert
Vdq			Daspoort	Quartzite
Vst			Strubenkop	Shale in places ferruginous
Vha			Hekpoort	Volcanic rock
Vb			Boshoek	Quartzite
Vt			Timeball Hill	Shale, siltstone,

Code	Supergroup	Group	Formation		Description
					conglomerate in places and quartz
Vmd		Chuniespoort Group	Malmani Subgroup	Frisco	Chert-free dolomite
				Eccles	Dolomite and chert
				Lyttleton	Chert-poor dolomite
				Monte Christo	Chert-rich dolomite
				Oaktree	Chert-free dolomite
Vbr			Black Reef		Quartzite, conglomerate and shale
Z	-	-	Halfway House Granite		Granite-gneiss, granite in places; gneiss
S	-	-	-		Syenite
di	-	-	-		Diabase

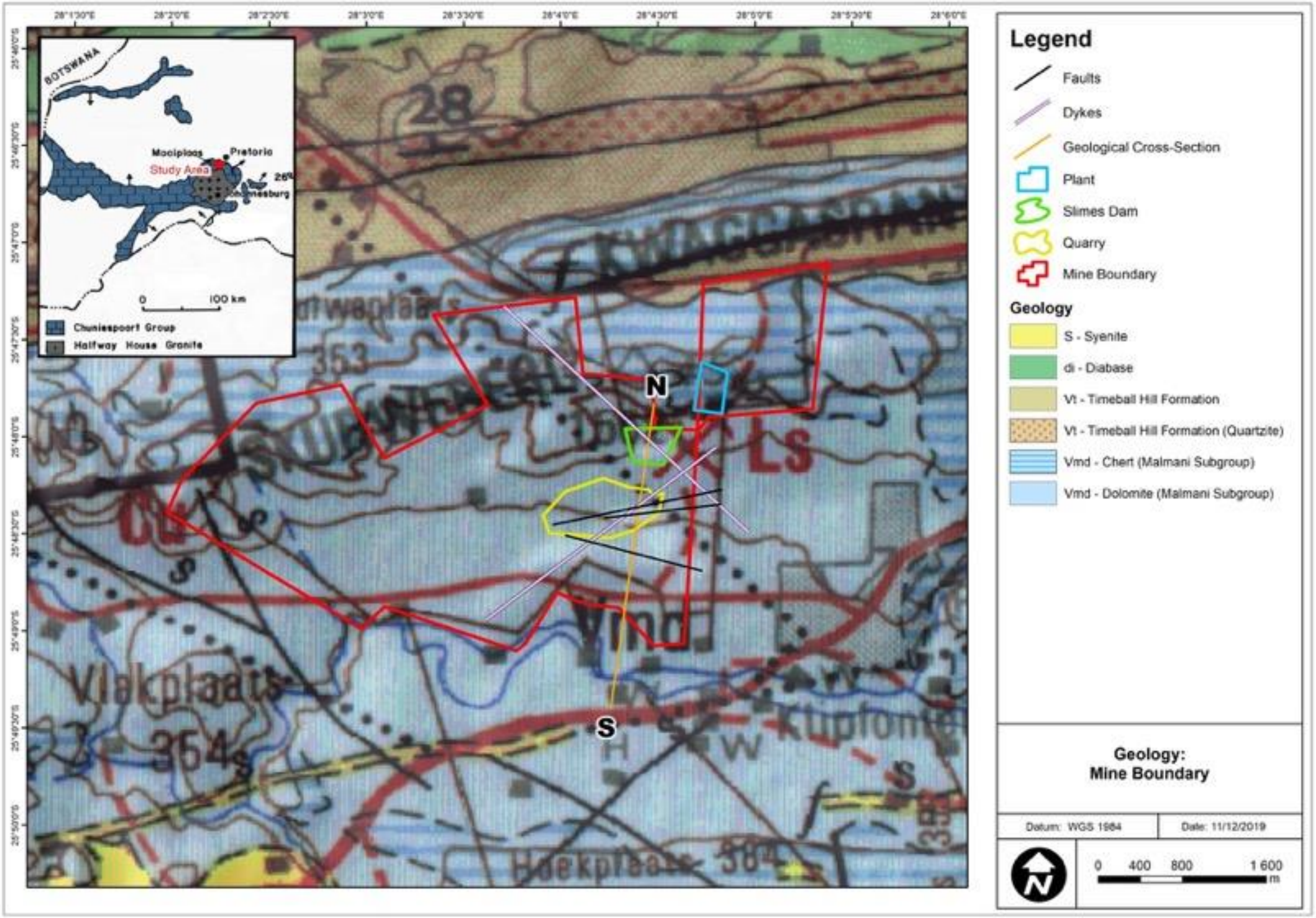


Figure 13: Geological map of study location (1:250 000-scale Geological Map Series 2528 Pretoria) with structural features and location with respect to Chuniespoort Group (adapted from Page and Du Plessis, 1986).

2.5. Structural features

Two normal faults are present on the northern boundary of the quarry and one on the southern boundary (**Figure 13**). According to drilling information, these faults are nearly vertical, and the displacement is approximately 50 m, and this is the only available information about the faults at the study area. A 12 m wide mafic dyke (**Figure 14**) was encountered cross-cutting the quarry and striking in a north-east direction. Another larger mafic dyke is known to occur north of the quarry but striking almost perpendicular to the other dyke in a north-west direction as depicted in **Figure 13**.

Figure 14: The 12 m wide mafic dyke cross-cutting quarry with lighter coloured alteration zones that can be seen on either side of the dyke. The alteration zones on either side lead into normal dolomite.

Stromatolites (structures related to the growth of microbial mats) are encountered in the walls of the quarry and range in diameter from 0.6 m to 1.8 m. Examples of some of these stromatolites can be seen in **Figure 15** and two of them are indicated with brackets.

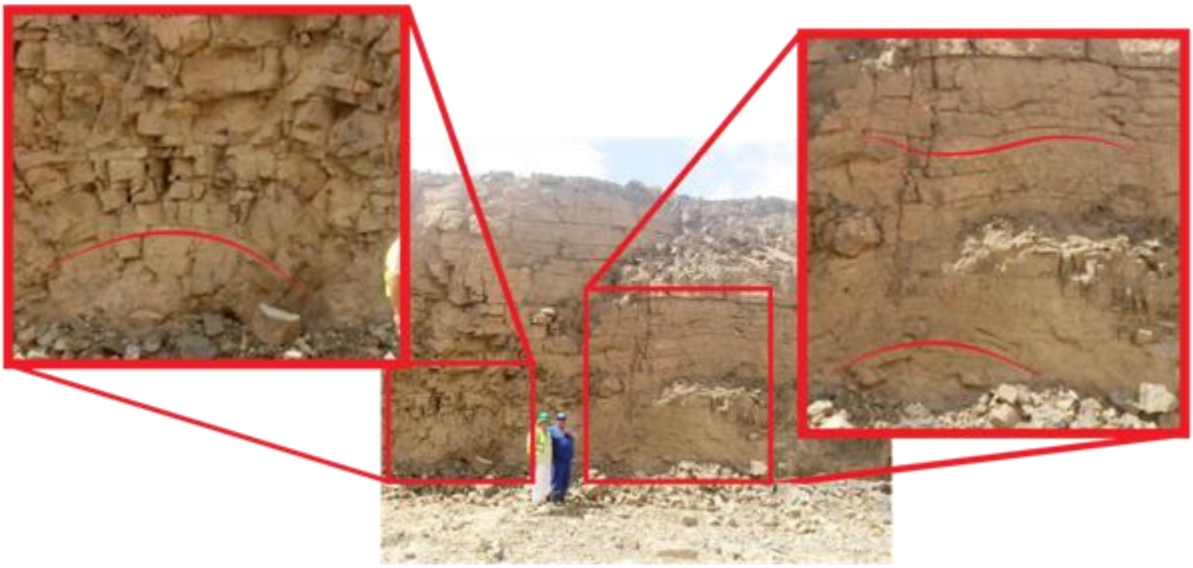


Figure 15: Stromatolites in the wall of the quarry, indicated with red lines on enlarged blocks of the picture.

The fresh dolomite is covered with transported material and weathered dolomite that varies in thickness from 0 – 30 m. The well-known pinnacles and grykes that are formed in dolomite terrain can be clearly seen on the upper walls of the quarry at PPC Mooiplaas **Figure 16**.

Figure 16: Transported material on the pinnacle and grykes that are formed in the weathered zone of the dolomite.

2.6. Geochemistry

A borehole named MA8 at PPC Mooiplaas was used by Page and Du Plessis (1989) to study the fluctuation of major chemical components vs. depth, **(Figure 17)**. CaO and MgO are relatively homogenous and show little variation through the Lyttleton Formation, but a clear decrease in CaO and MgO content is seen within the Monte Cristo Formation. CaO and MgO also decrease gradually towards the top of the Lyttleton and the Eccles Formation, but to a smaller extent. The $CaCO_3$/$MgCO_3$ ratio is very homogenous indicating that the dolomite is geochemically consistent.

Silica has an inverse relation to CaO and MgO and this is due to an increase in chert in the dolomite. Mica and clay minerals are generally present in very low quantities and only contribute a very small percentage of the silica content. Iron oxide is present in the dolomite between 0.5 % – 1.6 % with the Lyttleton Formation on the lower end and the Monte Cristo Formation on the higher end due to its increase in clay minerals (Button, 1975). The MnO in the Monte Christo Formation is the lowest at 0.4 % – 0.5 % but the MnO increases gradually upwards into the Lyttleton Formation to 1.2 % – 1.3 % and then decreases again towards the Eccles Formation to 0.5 % – 0.7 %.

Other oxides like Al_2O_3, TiO_2 and K_2O are present in low concentrations. Even with these low concentrations, the TiO and Al_2O_3 show an increase in the clay-bearing Monte Cristo

Formation relative to the other formations. Na_2O and P_2O_5 and S were only analysed on composite samples of the metallurgical zone and are present in concentrations between 0.003 % – 0.044 %.

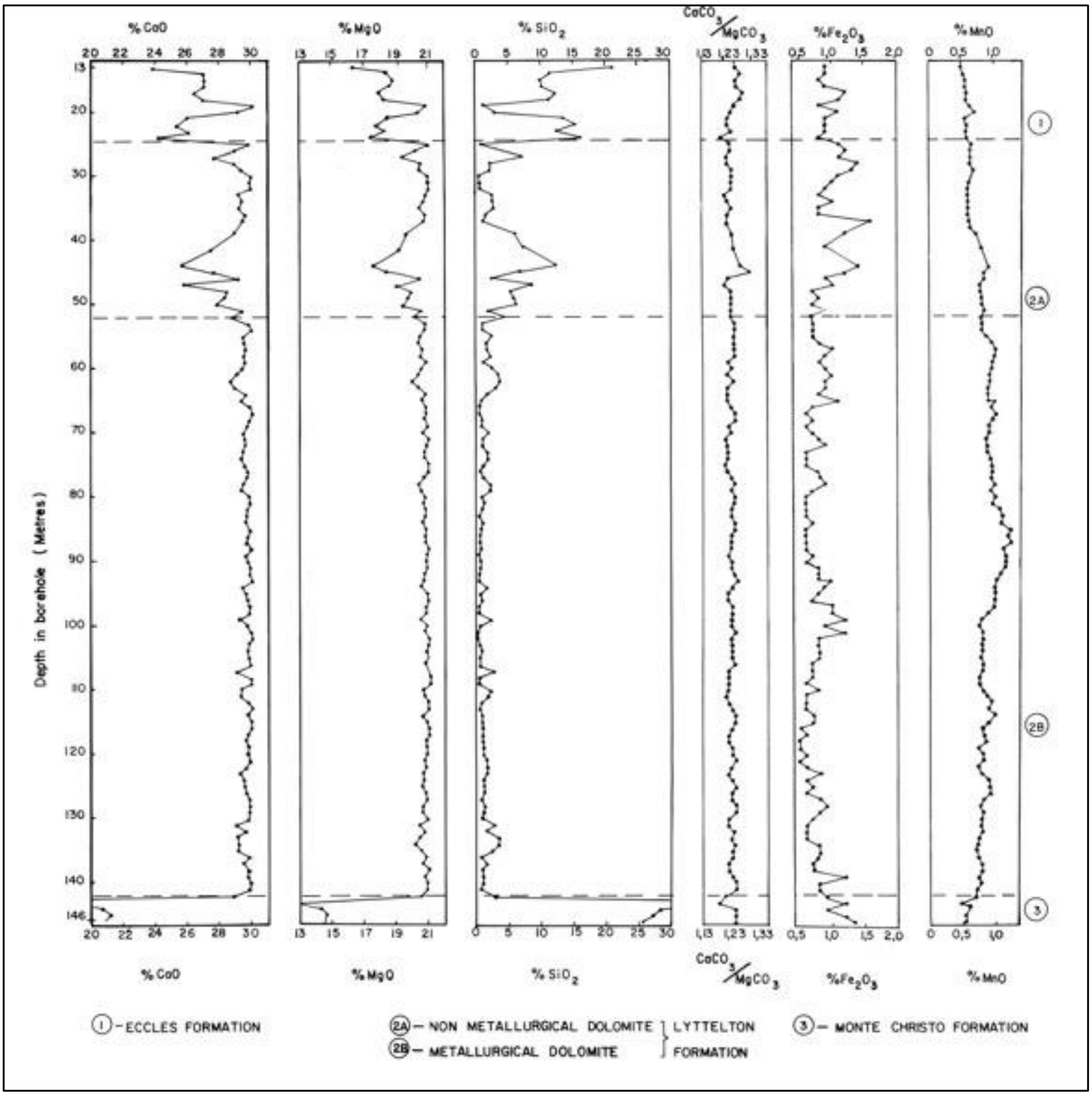


Figure 17: Chemical variation in the dolomite sequence at PPC Mooiplaas (Page and Du Plessis, 1986).

2.7. Hydrology

PPC Mooiplaas is part of the quaternary catchments A23D, A21H and A21B. The main mining activity takes place on quaternary catchment A21B. The Hennops River passes approximately 1 km south of the southern boundary of the mine and flows for approximately 24 km west, where it joins the Jukskei River. The combined river systems flow for another 13 km northwest into the Hartbeespoort Dam (**Figure 18**).

2.8. Regional hydrogeology

The aquifer yield and aquifer quality classifications were inferred from regional datasets and therefore only providing an indication of the conditions to be expected.

2.8.1. Aquifer type and yield

According to the 1:500 000 scale groundwater map of Pretoria (2528), the study area hosts a karst aquifer which means that open cavities and possibly even caves develop below ground level due to the dissolution of the dolomite (Meyer, 2014). This dissolution gives the aquifer enhanced properties of groundwater storage and permeability, and an average estimated borehole yield of 5 L/s is expected (**Figure 18**) (DWAF, 2005). To the south of the study area is an intergranular aquifer and to the north is mainly a fractured aquifer.

2.8.2. Aquifer quality

Electrical conductivity (EC) is a measure of the ability of the groundwater to conduct electricity and this is directly related to the concentration of ions in the water. Therefore, this parameter can be used as an indication of the quality of the groundwater.

The groundwater quality map of PPC Mooiplaas seen in **Figure 19** uses electrical conductivity (EC) to indicate the quality of a region's groundwater. The quality indicated for PPC Mooiplaas is 0 – 70 mS/m with a section just south of the study area with a quality of 70 – 300 mS/m (DWAF, 2005).

2.8.3. Aquifer vulnerability

The national scale groundwater vulnerability map of South Africa (Conrad and Munch, 2007), which was developed according to the DRASTIC methodology (Aller et al, 1987), shows that the study area has a high vulnerability to surface based contaminants (**Figure** 20).

The DRASTIC method takes the following factors into account:

D = depth to groundwater (5)
R = recharge (4)
A = aquifer media (3)
S = soil type (2)
T = topography (1)
I = impact of the vadose zone (5)
C = conductivity (hydraulic) (3)

The number that is indicated in the parenthesis at the end of each factor is the weighting of that factor specific to the study area.

The high vulnerability rating is most likely associated with the karst aquifer, due to the fact that surface pollutants can move relatively quickly into the groundwater via sinkholes and other features in karst environments, since these features provide a direct route for surface water into the subsurface.

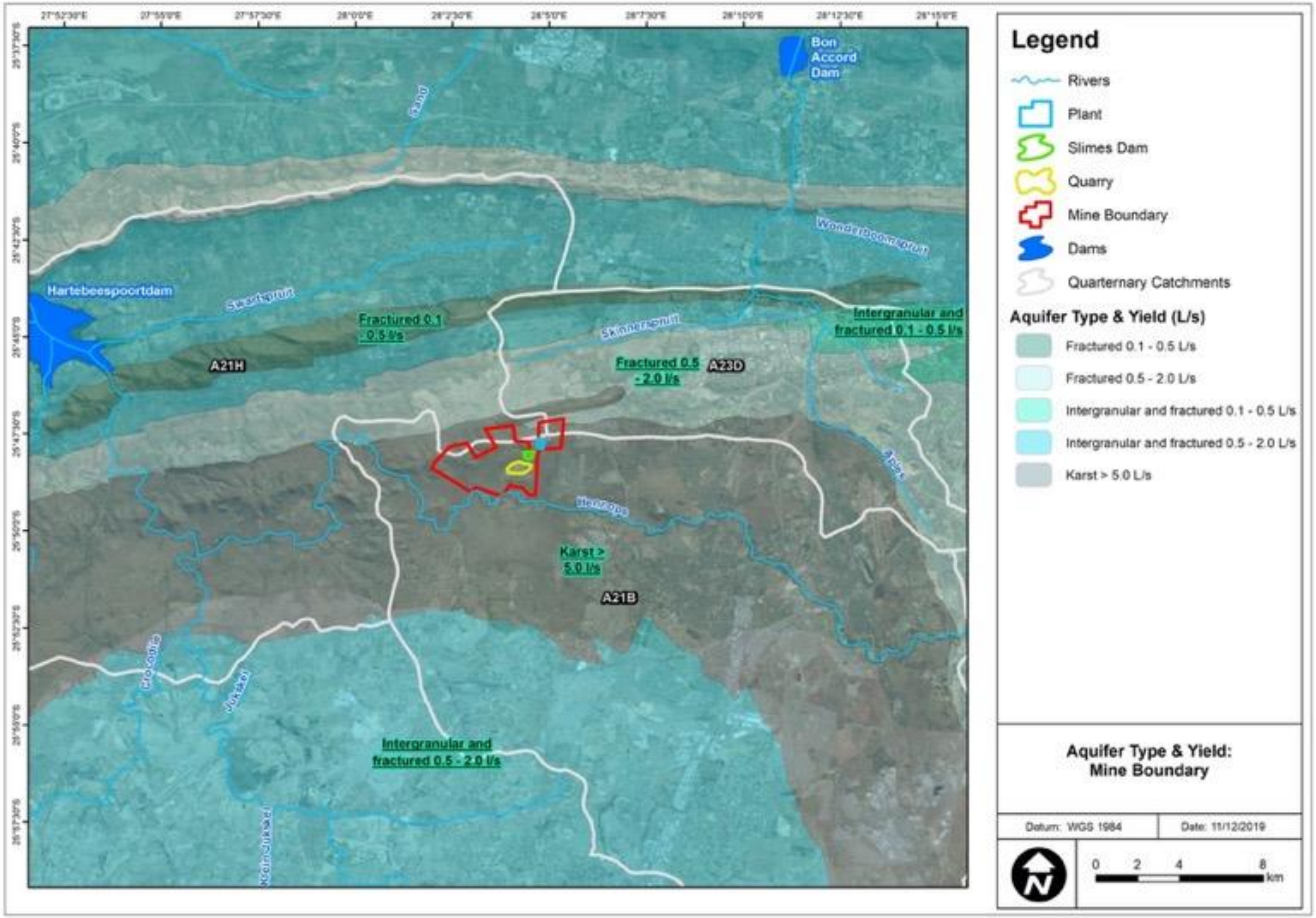


Figure 18: Regional aquifer type and yield from the 1:500 000 scale groundwater map (2528 – Pretoria) (DWAF, 2005) showing quaternary catchments, rivers, mine, quarry, slimes dam and plant extent.

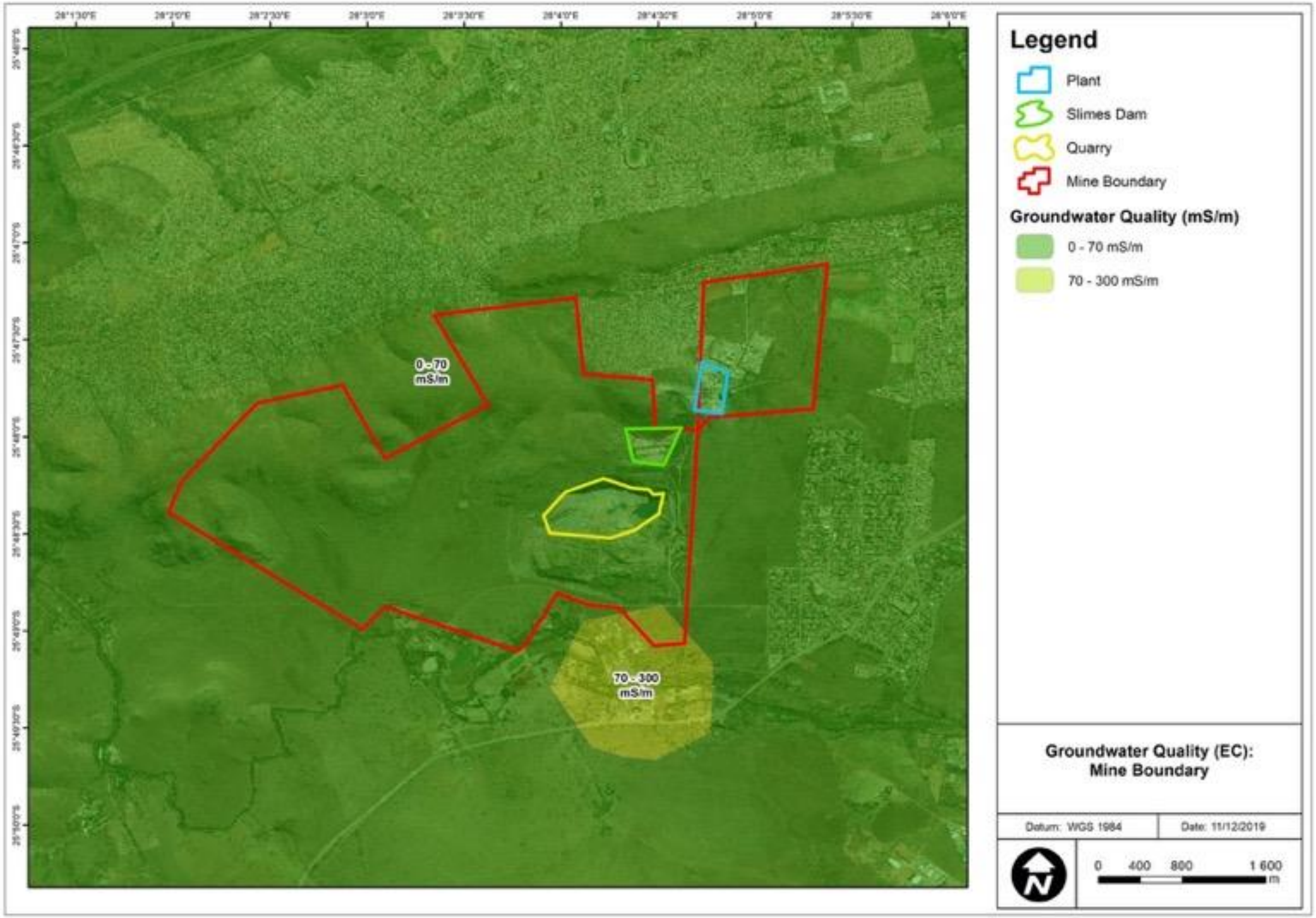


Figure 19: Regional groundwater quality shown with EC (mS/m) from (DWAF, 2005), showing the mine border, quarry, slimes dam and plant extent.

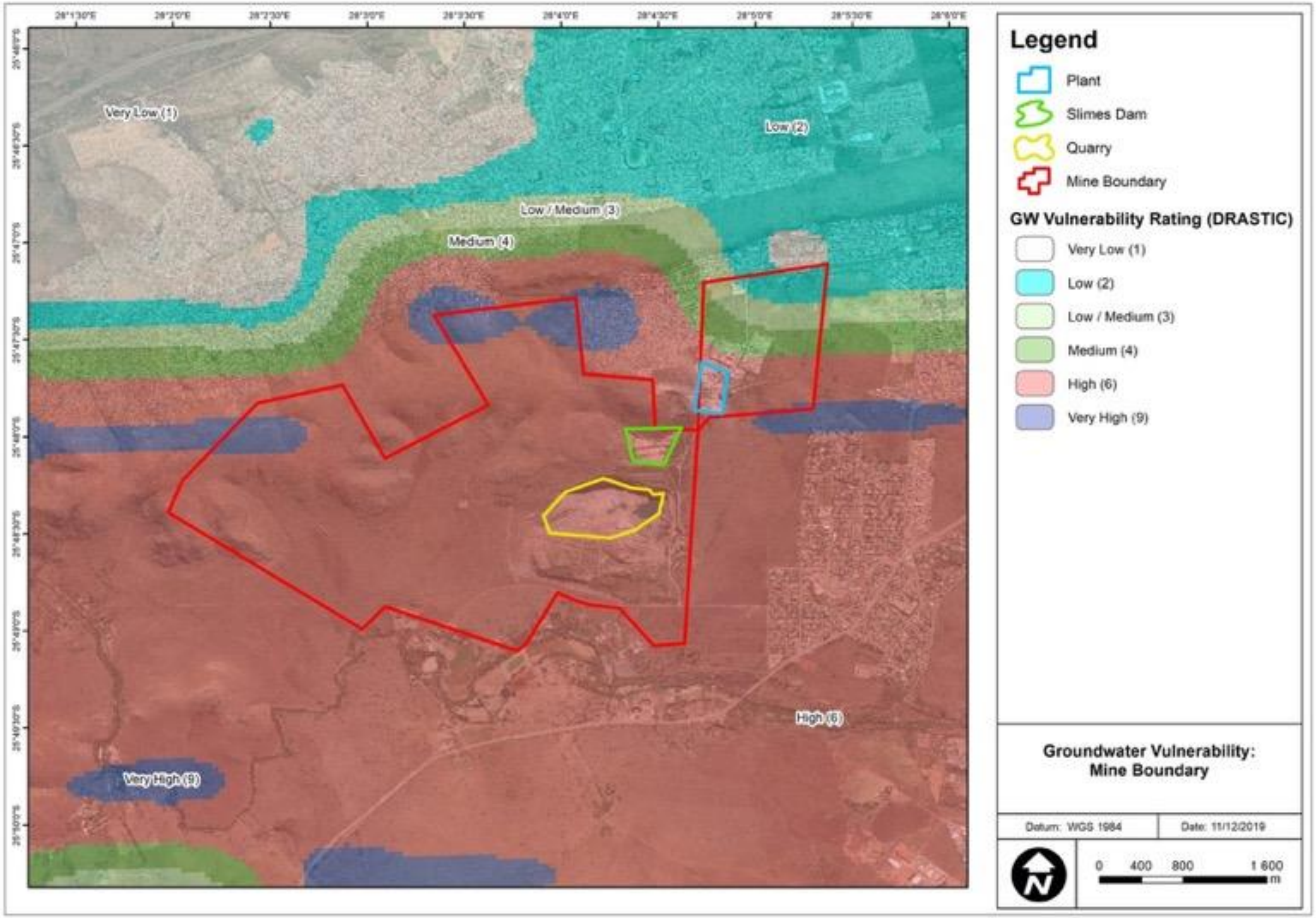


Figure 20: Regional groundwater vulnerability for the study area (DWAF, 2005), showing the mine, quarry, slimes dam and plants extent.

2.8.4. Compartmentalisation

The karst aquifers of the Chuniespoort Group are compartmentalised by several dykes intersecting the dolomite. The dykes are generally composed of pre-Karoo age dolerite and syenite (Meyer, 2014) result in barriers for the flow of groundwater. The study area is located on two compartments, named the Alwynkop and Laudium compartments. The dyke that separates the Alwynkop and Laudium compartment is the dyke that is known to occur just north of the quarry with a north-east strike. The second dyke is encountered in the quarry with a north-west strike and is 12 m thick, which also serves as a barrier for flow between the east and west pits in the quarry (**Figure 14**). Groundwater levels frequently vary from one compartment to the other, due to the dykes.

The groundwater levels mimic the topography, with a 90% (**Figure 21**) correlation factor resulting in the groundwater table being deeper below the Schurweberg ridge to the north of the pit and lower towards the Hennops River (GCS, 2008). However, this is in contrast with what literature indicates, which is that in a karst environment groundwater levels rarely mimic the topography. Meyer (2014) and Barnard (2000) describes the groundwater level in a karst environment as nearly horizontal with a low gradient which is an indication of highly permeable formations.

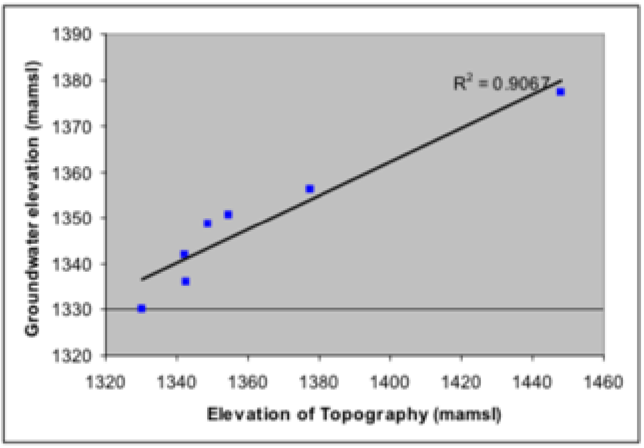


Figure 21: Groundwater vs. topography trend graph (from GCS, 2008)

Currently no pumping test or other surveys are known to assist in providing a better understanding of the hydrogeology of the study area. The quarry on the study area extends below the regional static water level, resulting in wall seeps on the northern and southern walls of the quarry and in the south-west corner of the quarry. An example of one of the wall seeps can be seen in **Figure 23.** The water that is used to wash the dolomite product forms a slurry which is deposited in the slurry dams. The slurry dam is located just north of the quarry and is most likely the cause of the wall leaks on the northern face of the quarry.

2.9. Previous work

The PPC Mooiplaas Mine came into operation in 1959. Therefore, a lot of geological reports and research have been done on the site. The mine has too much water thus some hydrological studies have also been done. Then lastly, to maintain a water use licence, the mine needs to monitor their groundwater monthly. This groundwater monitoring is done by Aquatico and the data from the monitoring was obtained for this study.

Table 2: List of environmental studies done on the site.

Date	Report name	Description and author
1986	Chert-free Metallurgical grade dolomite in the southern Transvaal: The Mooiplaas and Glen Douglas mines.	Article by D.C. Page and P.G. du Plessis
December 2008	Hydrological assessment	Groundwater Consulting Services (GCS)
November 2010	Environmental Impact Assessment	Umhlaba Environmental Consulting
June 2013	Groundwater Quality Assessment	Groundwater Complete Consulting
August 2014	Groundwater Quality Assessment	Groundwater Complete Consulting
February 2015	Groundwater Quality Assessment	Groundwater Complete Consulting
December 2015	Groundwater report	Groundwater Complete Consulting
January 2017	Groundwater Quality Assessment	Groundwater Complete Consulting

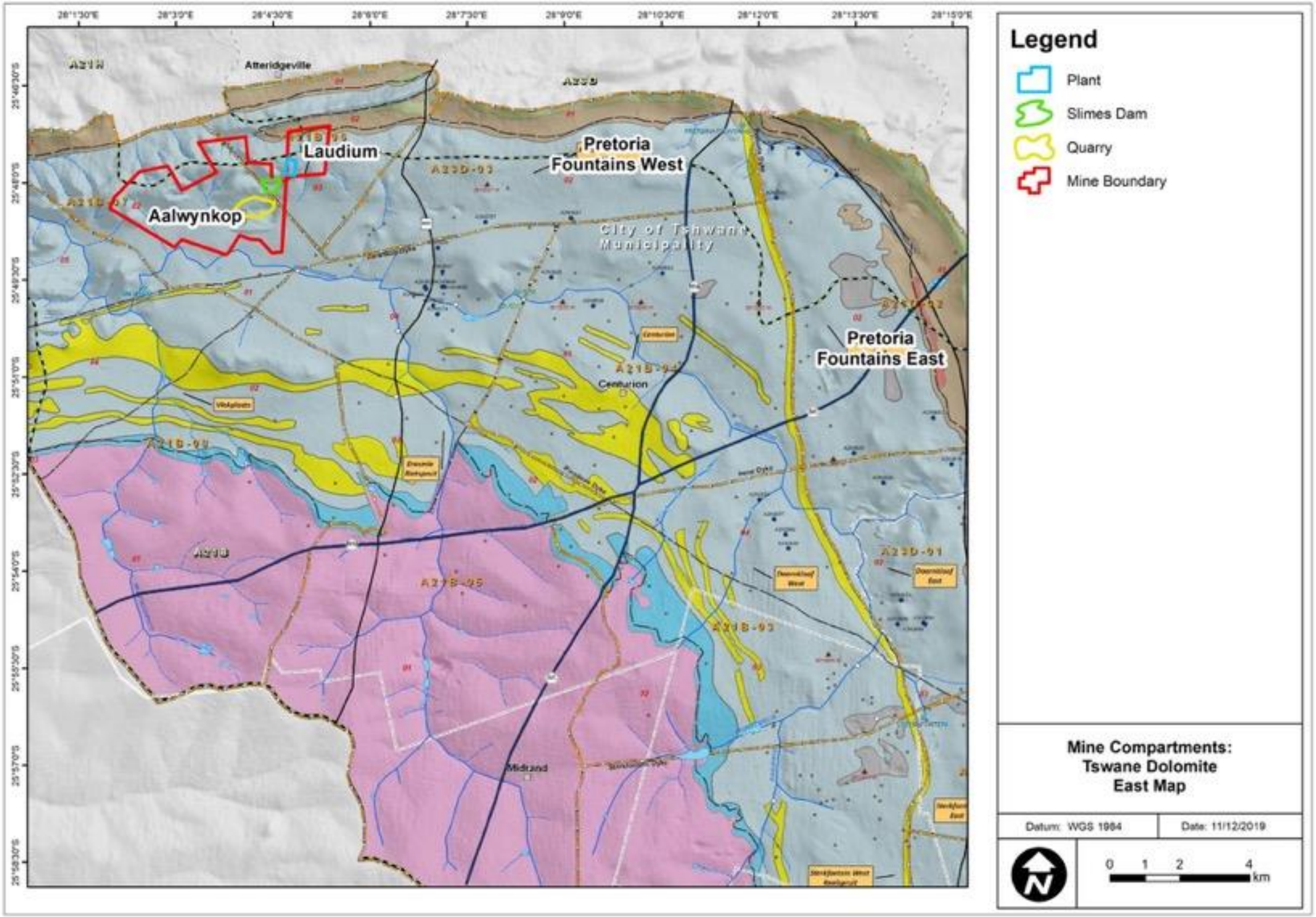


Figure 22: Hydrogeological compartments of the study area (Meyer, 2014) showing the Alwynkop, Laudium, Pretoria Fountains West and Pretoria Fountains East compartments. The mine, quarry, slimes dam and plant extent are also shown.

Figure 23: Dark marks on the northern pit wall indicating water seeping into the pit.

2.10. Conceptual model

A conceptual model was developed, based on the literature review and information obtained from the mine. The conceptual model will provide an understanding of the mining operations, hydrology and hydrogeology. To assist in explaining the conceptual model **Figure 24** a flow diagram and **Figure 25** a cross section were developed.

2.10.1. Mining activity

PPC Mooiplaas is a dolomite quarry where the rock is transported with a conveyor belt to the plant area at the top of the Skurweberg ridge. This is where the dolomite is split into two groups: the SiO_2-rich and the SiO_2-poor dolomite. The SiO_2-poor dolomite is known as metallurgical grade and is moved to the MDV plant [Metallurgical Dolomite Crusher (Metallurgiese Dolomiet Vergryser)] where the rock is crushed, washed and sold to the steel industry where it is used as flux. The SiO_2-rich dolomite rock is sent to the normal plant where it is crushed to different sizes, washed and then sold to other industries like the construction industry or agricultural industry. The washing process results in a slurry which is pumped to the slimes dams, where the fine particles settle to the bottom and the water either seeps into the vadose zone or evaporates. One significant difference between the MDV plant and the normal plant is that a flocculant is added to the slurry water of the normal plant but not to the slurry water of the MDV plant. The purpose of the flocculant is to help the fine particles in the water settle to the bottom of the water body. After the water has sufficiently drained or evaporated from the slimes dam, the fines are mined and sold as agricultural or powdered lime products. The water chemistry in the study area has several influences and sources, and the main purpose of this study is to investigate what the movement of the water in this study area and how it is influenced by its environment.

2.10.2. Pumped water

A flow diagram of the pumped, natural and inferred waterflow can be seen in **Figure 24**. This diagram shows how the water is pumped from the West Pit (WP) to the East Pit (EP) and then from the EP to the Plant Inlet (PI). The mine also uses the Fish Dam (FD) as storage for the water and therefore, it is pumped in and out of the FD from the EP. At the plant area, the SiO_2-rich and the SiO_2-poor dolomite is washed separately, and the slurry water generated from the washing process is collected in concrete dams at the plant. From the plant, the slurry water is pumped towards the slimes dams (SsD) where the water either evaporates or percolates into the subsurface.

2.10.3. Natural movement of water

During the site visits it was observed that water seeps in from the northern wall of the quarry. These water seeps were observed on the west and east side of dyke 2 that crosscuts the quarry. The West Pit Wall Seep (WPWS) was much larger in extent with regards to the amount of water that seeps out of the wall, than the East Pit Wall Seep (EPWS). Water also percolates through the vadose zone towards the EP from the FD. On the west side of the WP a seep was also found and sampled when possible. The last natural water flow observed during the site visits was water that runs from the artesian borehole Groundwater Flow 13 (GWF13) towards the EP.

2.10.4. Water levels

The water levels in an aquifer usually mimic the topography in the area (**Figure 21**). Below the Skurweberg ridge, the water levels are a lot deeper compared to down gradient closer to the Hennops River, as seen in **Figure 25**. Therefore, the groundwater flow direction is from the higher lying Skurweberg ridge towards the lower lying Hennops River (GCS, 2008).

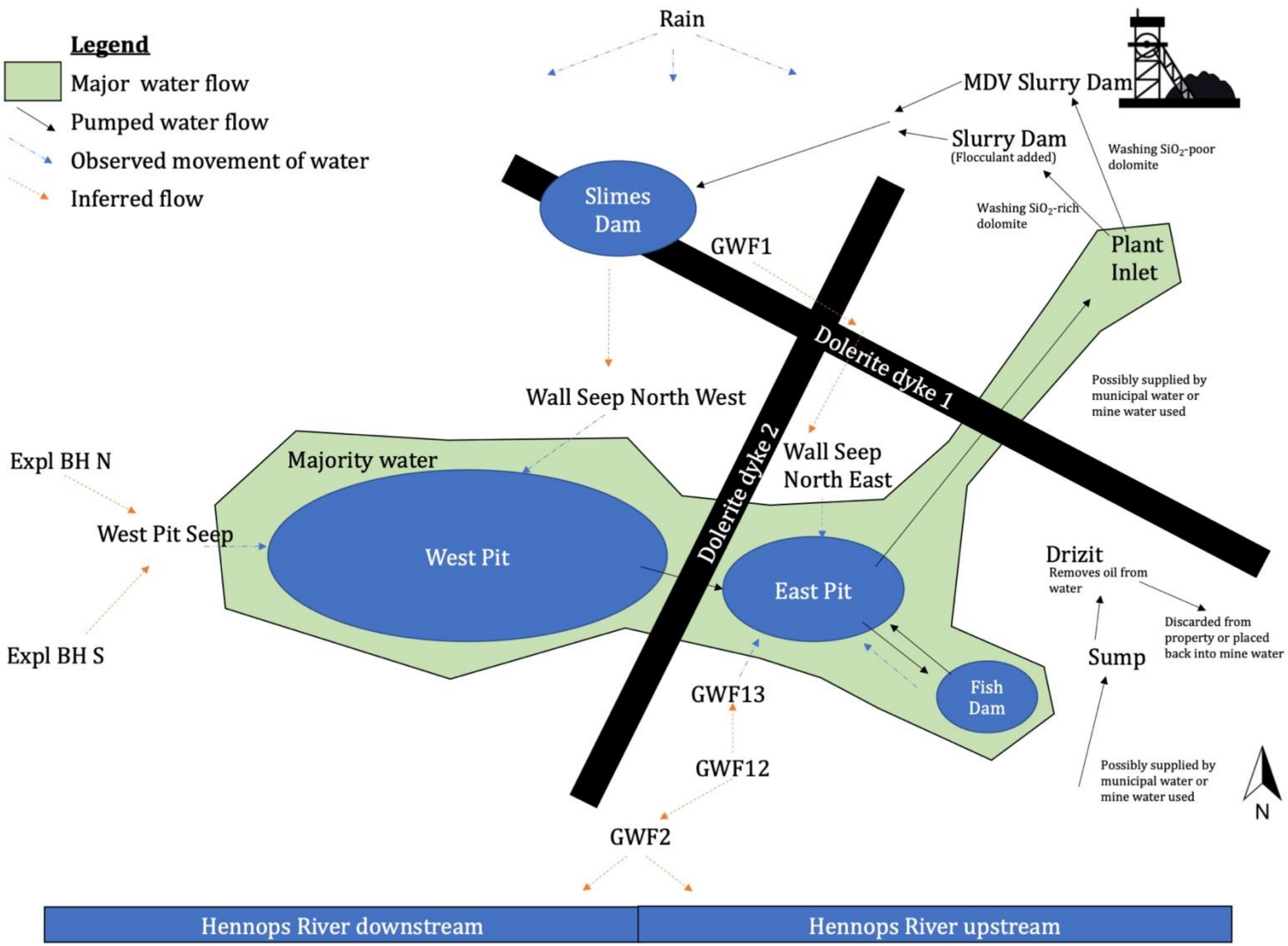


Figure 24: A schematic and conceptual diagram depicting the water movement in the study area.

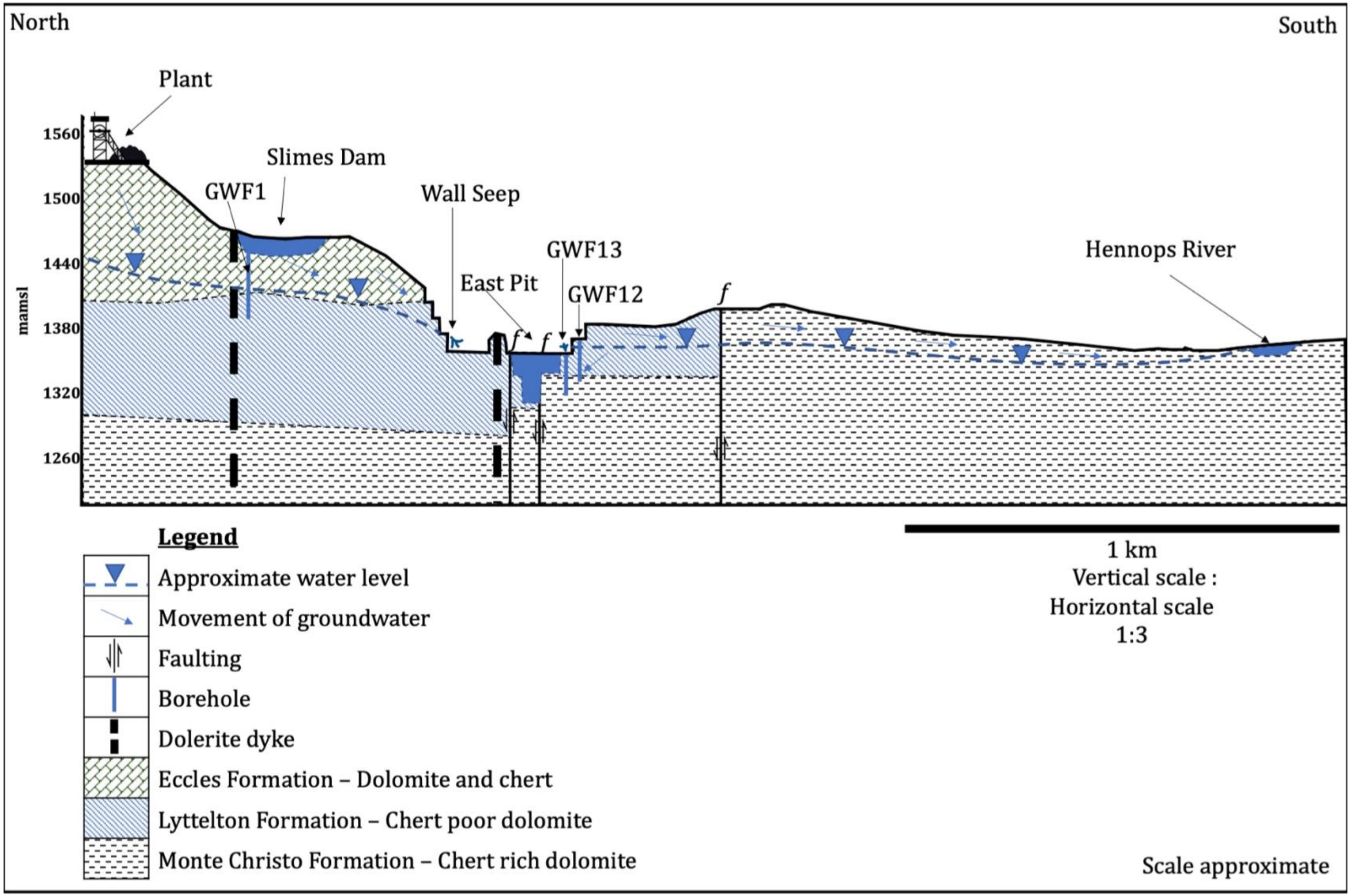


Figure 25: A schematic and conceptual north-south hydrogeological section (adopted from Page and Du Plessis, 1986).

3. Methods

3.1. Sampling locations

Water samples from several water bodies in the study area were sampled monthly from April 2017 until September 2017. Rainwater was also sampled in Monument Park, Pretoria, 15 km east of the study area (see **Figure 9** in Chapter 2) from December 2016 until May 2018. The onsite sampling locations are displayed in **Figure 26** and more information on the sampling locations can be found in **Appendix A**.

3.2. Sampling methods

3.2.1. Rainwater

A rain gauge was used for measuring and collecting rainwater samples. In addition to the rain gauge two 20 L buckets were used for ensuring enough sample could be collected for analysis as seen in **Appendix A**. The advantage of a simple rain gauge is that it is well calibrated by national weather services and no other equipment is required. However, the disadvantage of a rain gauge and the two 20 L buckets are that they require daily operation and there is a risk of evaporation if the sample is not taken shortly after the rainfall. Therefore, the lids of the buckets were shaped to a cone with a slit in to cover the bucket and the sampling of the rainwater took place as soon as possible after it rained. There was also a risk of interaction between water and air in the sampling bottle during storage, but this risk was minimised by keeping the sample in a fridge until analysis and by filling the bottles with no headspace.

The sampling location the rainwater was in Monument Park, Pretoria, 15 km east of the study area (see **Figure 9** in Chapter 2), which allowed easy and nearby access to the rain meter. This enabled more accurate and reliable sampling at a low cost. The rain was sampled each time after the rain fell from December 2016 until May 2018, and composite monthly samples were analysed for major chemical components and stable isotopes.

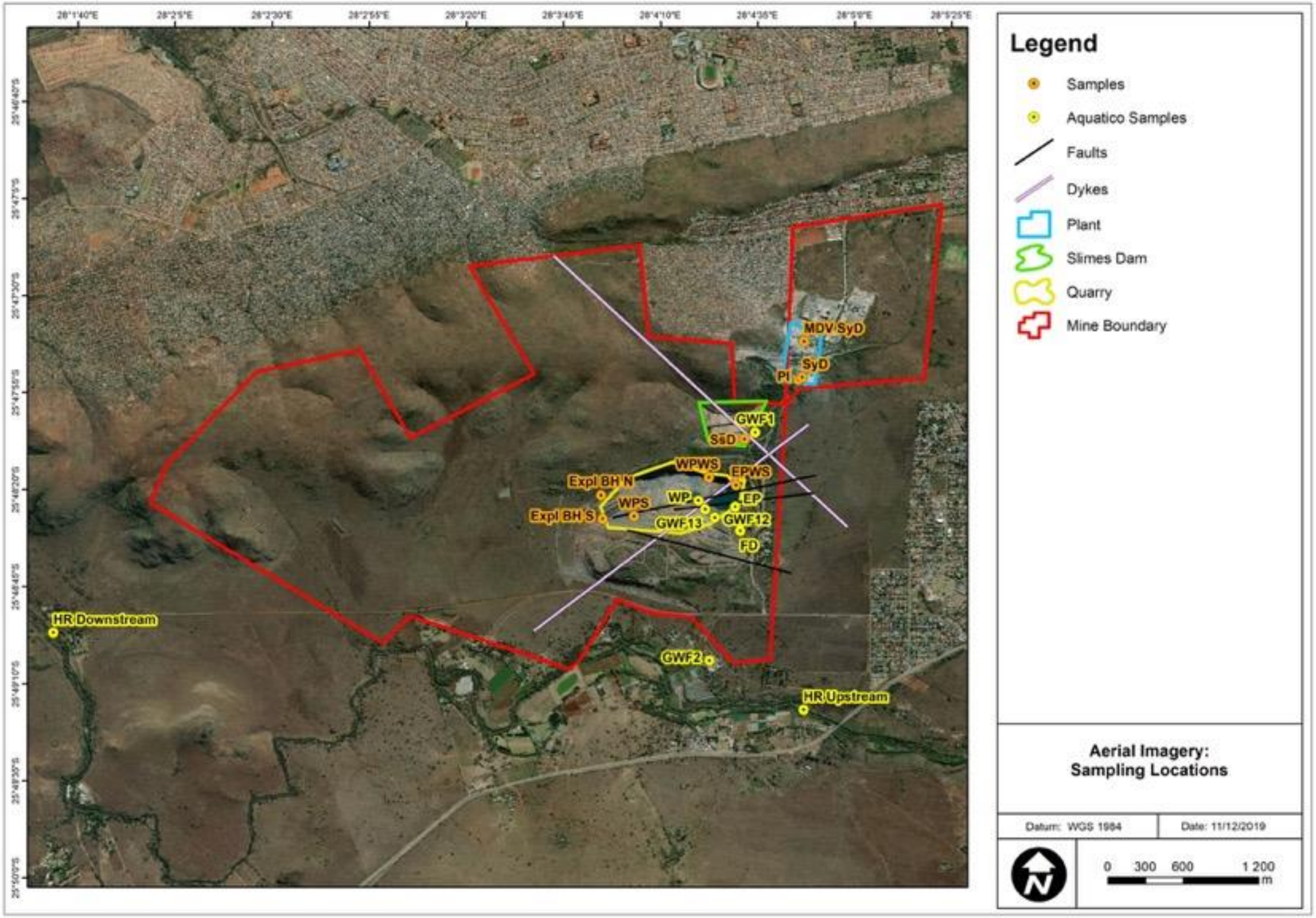


Figure 26: The study area, Aquatico monitoring points, sampling locations (please refer to the glossary for explanations of the acronyms), dykes and faulting positions superimposed on an aerial photograph.

3.2.2. Phreatic zone

The groundwater of PPC Mooiplaas is sampled monthly by Aquatico through the use of a bailer, with no purging. The same two boreholes Aquatico sample monthly were sampled for the phreatic zone (Groundwater Flow 1 (GWF1) and Groundwater Flow 12 (GWF12)) including two water containing exploration boreholes. The two Exploration Boreholes had a foul rotten egg smell and fur was encountered on the bailer while sampling.

During the planning stages of the study it was theorised that purging the boreholes would not be necessary because the quarry is dewatered resulting in a high-water table gradient surrounding the pit, which will cause the water to move through the borehole instead of staying stagnant. This theory had to be tested by doing a purge on the first sample run as seen in **Figure 27**. Purging was done with a pump that can be lowered into a borehole up to 100 m with the following steps:

GWF1

- Purging information and calculations were made as seen in **Table 3**.
- The pump was installed to 100 m.
- The borehole was purged to 100 m three times.
- The pump was removed, and a sample was taken by a bailer.

GWF12

- Purging information and calculations were made as seen in **Table 3**.
- The pump was installed to 40 m like **Figure 28**.
- The borehole was purged for 40 minutes to remove the volume of stagnant water.
- The pump was removed, and a sample was taken by a bailer.

Exploration boreholes

- The exploration boreholes were uncased, which could mean that the borehole could collapse should it be purged.
- No purging was done but a bailer was used to remove some water from the borehole before a sample was taken by a bailer.

Table 3: Borehole purging information.

	GWF1	**GWF12**
Water level (m)	~70	~4
Borehole depth (m)	~140	~89
Height of water column	70.19	85.22
Diameter of borehole (mm)	152	152
Volume of standing water (L)	1273.66	1546.39

Figure 27: Lowering of a pump in preparation of purging GWF12.

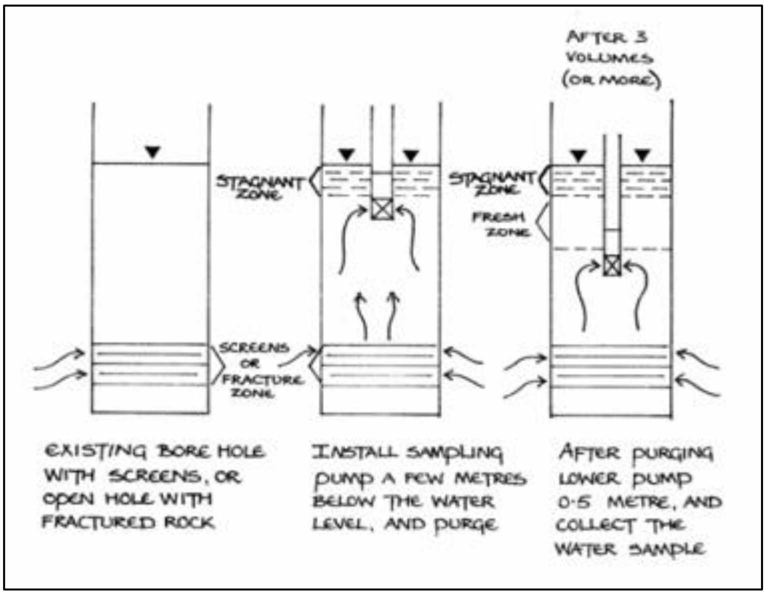


Figure 28: Sketch showing the positioning of a pump in the borehole (Weaver et al. 2007).

The depth of the boreholes made purging extremely expensive therefore, it required examination into whether it truly was necessary to purge every single sampling run. This was done by comparing the March 2017 chemistry analysis with that of the purged April 2017 chemistry analysis and the stable isotope data of the purged April 2017 results with the unpurged data of May 2017. It was found that the chemistry results of March 2017 and April 2017 and the isotopic results of April 2017 and May 2017 were very similar and therefore, to save costs during the rest of the sampling period, no purging was done.

3.2.3. Surface water

There were five main surface water sources that were sampled: the processing plant, slimes dam, fish dam and the two pit lakes of the quarry. Grab samples were taken by hand in plastic bottles of water at the surface at each water body.

3.2.4. Other samples

Three other sources of water were taken as samples. The first is the west pit seep (WPS): this is water that seeps episodically into the west pit in the south west corner of the west pit. The seep was sampled by using the cap of the sampling bottle to fill the sampling bottle. The last source are wall seeps that were sampled on the northern wall of the quarry. The one wall seep occurred on the west side of the dyke that transacts the quarry and the other wall seep occurred on the east side of the dyke. The flow of the water at this wall was high enough that a bottle could be placed or held beneath it as the drip filled it within 5-10 minutes.

3.2.5. Summary of samples taken

Table 4 contains a list of all the samples taken on a monthly basis form April 2017 to September 2017 and analysed for major ions and stable isotopes.

Table 4: Summary of all the samples.

Sampling point	Acronyms	Total number of samples
Plant Inlet	PI	6 + 1 duplicate
Slurry Dam	SyD	6 + 1 duplicate

Sampling point	Acronyms	Total number of samples
MDV Slurry Dam	MDV SyD	6
Slimes Dam	SsD	6
West Pit	WP	6 + 1 duplicate
East Pit	EP	6
Fish Dam	FD	6 + 1 duplicate
West Pit Seep	WPS	3
Exploration Borehole North	Expl BH N	2
Exploration Borehole South	Expl BH S	3
West Pit Wall Seep	WPWS	4 + 1 duplicate
East Pit Wall Seep	EPWS	3
Groundwater Flow 1	GWF 1	6
Groundwater Flow 12	GWF 12	6
Rainwater	-	6
	Total	80

3.3. Data

The data was obtained by using several different analytical methods, explained in detail in this section. All the data was examined to ensure that the quality of the data is sufficient for this study. The data validation methods are discussed in Chapter 3.3.8.

3.3.1. Inorganic chemistry

The historic data that was collected by Aquatico was used to determine what to analyse the water for. From the historic data one could see that heavy metals such as Fe, Al, Cr, Ni and other metals were always reported as below detection limit. Due to this low metal content in the water those elements were removed from the list of analytes, and the following analysis was done:

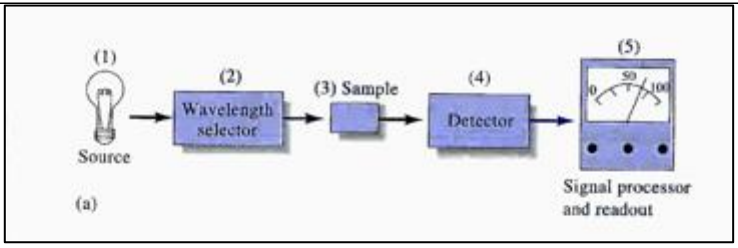
Table 5: Analyte and respective analysis method.

Analyte	Uncertainty of measurement (%)	Detection Limit (mg/L)	Standard	Method
Alkalinity	10.41	1.99	Sodium Carbonate	Automated spectrometry
Chloride (Cl^-)	11.39	0.557	Sodium Chloride	
Sulphate (SO_4^{2-})	9.39	0.141	Sodium Sulfate	
Orthophosphate (PO_4^{3-})	6.42	0.005	Potassium dihydrogen phosphate	
Ammonium (NH_4^+)	8.59	0.008	Ammonium chloride	
Nitrate (NO_3^-)	9.85	0.194	Sodium nitrate	
Fluoride (F^-)	10.11	0.263	Sodium fluoride	
Bromide (Br^-)	-	0.01	Sodium bromide	Spectrometry
Electrical conductivity (EC) @ 25°C	9.52	0.024	Sodium chloride	Potentiometric
pH @ 25°C	4.23		Buffer solutions of 4, 7 and 10	
Total Dissolved Solids (TDS)	9.42	10.2	-	Gravimetric
Total Hardness (TH)	-	-	-	Calculation
Calcium (Ca^{2+})	8.78	0.082	Custom multi element standard	Inductive Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)
Potassium (K^+)	12.05	0.015	Custom multi element standard	
Magnesium (Mg^{2+})	7.54	0.077	Custom multi element standard	
Sodium (Na^+)	7.96	0.041	Custom multi element standard	

The chemical analysis was done by Aquatico who uses an automated spectrophotometer to analyse for alkalinity, Cl, SO_4, PO_4, NH_4, Br and NO_3. The metals Ca, K, Mg and Na were analysed by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy).

3.3.2. Spectrometry

Spectrometry instruments use ultraviolet, visible or infrared light and therefore, it is frequently referred to as an optical instrument. Most spectroscopic instruments are made up of five components: (1) a source of radiant energy; (2) a wavelength selector that can isolate specific regions of the light spectrum; (3) sample container/s; (4) a detector that can convert the light signal into a measurable electrical signal; (5) a signal processing readout unit that is usually a computer in modern instruments (Skoog et al., 2004). **Figure 29a** illustrates the configuration of these five components in a spectroscopic instrument. Alkalinity, Cl, SO_4, PO_4, NH_4 and NO_3 were analysed with an automated KoneLab instrument as seen in **Figure 29b**. The bromide analysis used is extremely long and very time dependent therefore, the desktop Hach spectrophotometer instrument was used instead, as seen in **Figure 29c**. The sample containers used with these instruments are called cuvettes which are translucent holders where the sample and reagents are pipetted into for the reaction to take place before the measurement is taken. The main difference between the KoneLab automated spectrophotometer and the Hach manual spectrophotometer is the size of the cuvettes and the amount of sample and reagent that is required. With the KoneLab, the sample and reagents are pipetted into very small cuvettes which are approximately 15mm*7mm*2mm in size with 12 in a single cell as seen in **Figure 30a-f**. The KoneLab also uses automated syringes to pipette the sample and the reagents into the cuvettes. With the Hach, the sample and reagents are pipetted into much larger cuvettes (see **Figure 30g**) with a handheld pipette.



(a) The arrangement of an absorption measurement instrument.

(b) Automated spectrophotometric instrument.

(c) Manual spectrophotometric instruments.

Figure 29: Spectrophotometry instrument design and some of the different spectrometers used (Skoog et al, 2004).

Alkalinity

Alkalinity in water is a measure of the acid-neutralizing capacity of the water and can also be an indication of base content. Ions that contribute to alkalinity are bicarbonate (HCO_3^-), carbonate (CO_3^{-2}), hydroxide (OH^-) (at high pH values), and several others but to a much lesser extent. The principal of this analysis is that an indicator, methyl orange is added to the sample, after which the sample is titrated with an acid that will lower the pH of the sample to 3.1, at which point a colour change will occur due to the methyl orange indicator. This change in colour is measured by the automated spectrometer at 540 nm and it is proportional to the alkalinity in the sample (APHA, 2005).

Chloride (Cl)

Chloride is measured in the form of Cl^- and is a halide like bromide. The principal for this analysis is that chloride reacts with mercuric thiocyanate resulting in a mercuric chloride complex. This releases the thiocyanate which will react with iron (III) resulting in red ferric thiocyanate. The colour that is produced is proportional to the chloride concentration and this analysis is measured at 480 nm (APHA, 2005).

Sulphate (SO_4)

The principal for this analysis is that the sulphate ion is precipitated using a strong acid with barium chloride. The resulting turbidity is proportional to the amount of sulphates in the water (APHA, 2005).

Orthophosphate (PO_4)

Orthophosphate forms a complex with ammonium molybdate and antimony potassium tartrate under acidic conditions, and when reduced with ascorbic acid a blue colour is produced which is proportional to the amount of phosphate that can be measured photometricly at 880 nm (or 660 nm) (APHA, 2005).

Ammonium (NH_4)

Ammonia reacts with hypochlorite ions due to the alkaline hydrolysis of sodium dichlorocyanurate and sodium salicylate at a pH of 12.6. This is also done in the presence of sodium nitroprusside to form a blue compound. This colour is proportional to the amount of ammonia in the sample and is measured at 660 nm (APHA, 2005).

Nitrate (NO_3)

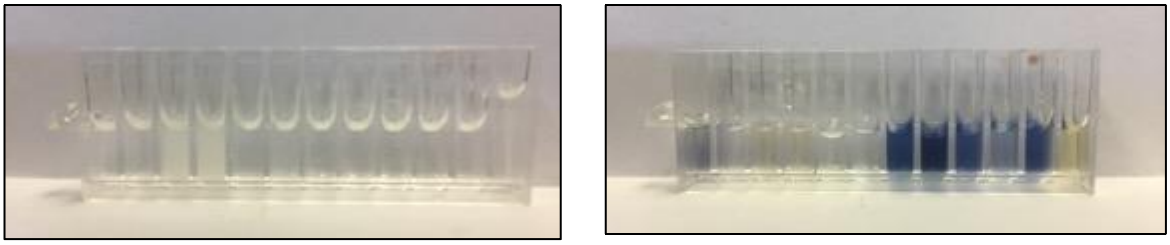
Nitrate is reduced to nitrite with hydrazine sulphate. The nitrite produced is determined by diazotisation with sulphanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride. The colour is measured at 540 nm (APHA, 2005).

Bromide (Br)

The principal of the bromide analysis is to treat the sample with chloramine T, in the presence of phenol red, resulting in the oxidation of bromide and bromination of phenol red. Then the sample is buffered to a pH of 4.5 to 4.7, turning it into a violet colour that is proportional to the amount of bromide in the sample (APHA, 2005).

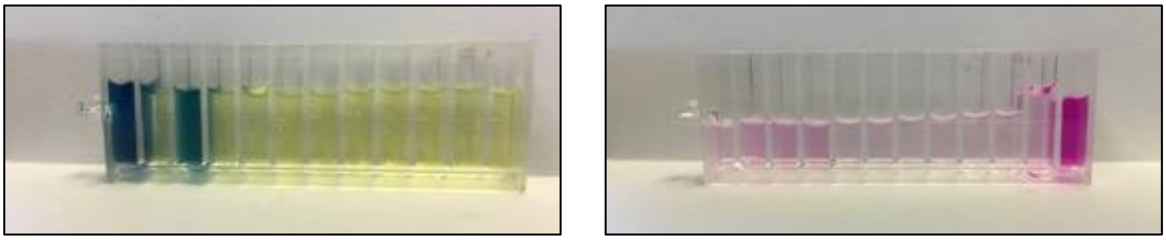
(a) Alkalinity – alkalinity is titrated to a specific point therefore, the alkalinity analysis all has the same colour unless the sample has an overpowering colour.

(b) Chloride – the deeper orange the colour the more chloride is in the sample.



(c) Sulphate – the more turbid the sample the more sulphate is in the sample.

(d) Orthophosphate – the bluer the sample turns the more orthophosphate is in the sample.



(e) Ammonium – the bluer the sample the more ammonium is in the sample and yellow means there is not any ammonia in the sample.

(f) Nitrate - the pinker the sample the more nitrate is in the sample.

(g) Bromide – the deeper purple the colour the more Br is present in the samle.

Figure 30: Pictures showing the cuvettes after analysis on water samples.

3.3.3. Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)

With optical emission spectroscopy, the sample is excited by an external energy source in the form of heat, electrical energy or several others. In the case of an ICP-OES, the sample is excited by the heat of an inductively coupled plasma that has temperatures of about 5 700 °C to 7 700 °C. **Figure 31** shows the emission process where in (a) the sample is excited and in (b) the energy level diagram shows with the upwards dashed lines of the individual atoms being excited from their ground states. The downward solid arrows show that after a few nanoseconds, the excited atoms relax again, resulting in a release of energy as photons. With this information, an emission spectrum can be made as seen in (c). The emission spectra diagram is a measure of radiant power emitted P_E as a function of wavelength, λ. This spectrum is unique for each element making it one of the commonly used methods for elemental analysis. A block diagram in **Figure 32** shows the arrangement of a typical ICP-OES (Skoog et al., 2004).

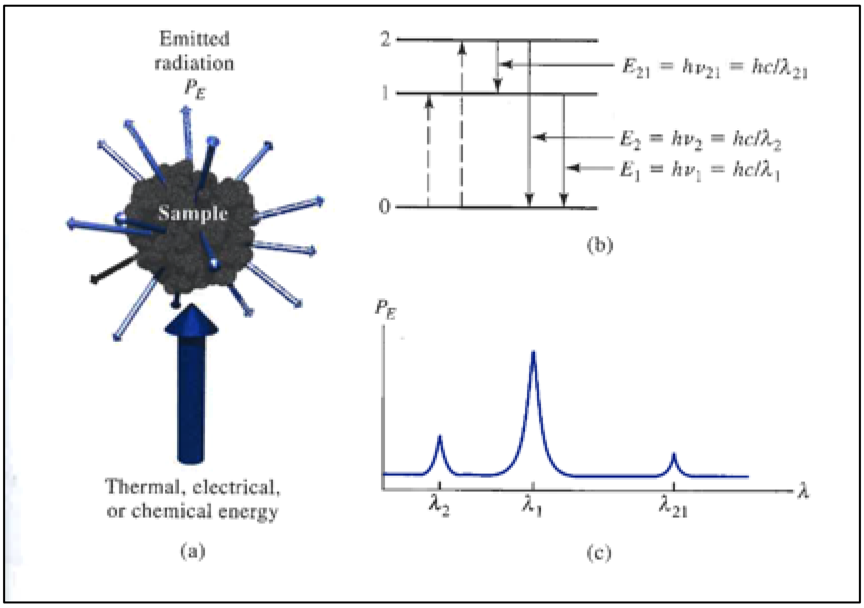


Figure 31: Emission process. In (a) it shows that the sample is excited by an energy source like in the case of an ICP-OES a plasma is used. In (b) the energy-level diagram the upwards dashed lines indicate the excitement of the analyte, and the downward solid lines indicate the loss of energy due to emission of photons. The diagram shown in (c) is the resulting spectrum shown as a measure of radiant power emitted P_E as a function of wavelength, λ (Skoog et al., 2004).

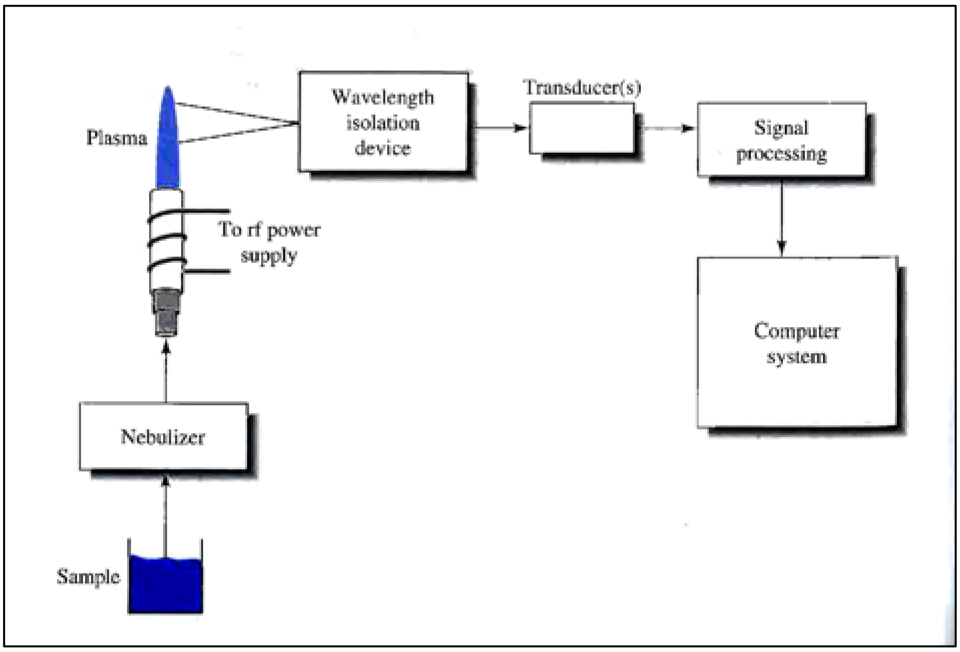


Figure 32: Block diagram of an ICP-OES (Skoog et al., 2004).

For this study, the ICP-OES method was used to analyse for Ca, K, Mg and Na. A Perkin Ekmer Optima 7300DV/Optima 8300 ICP-OES instrument shown in **Figure 33** was used.

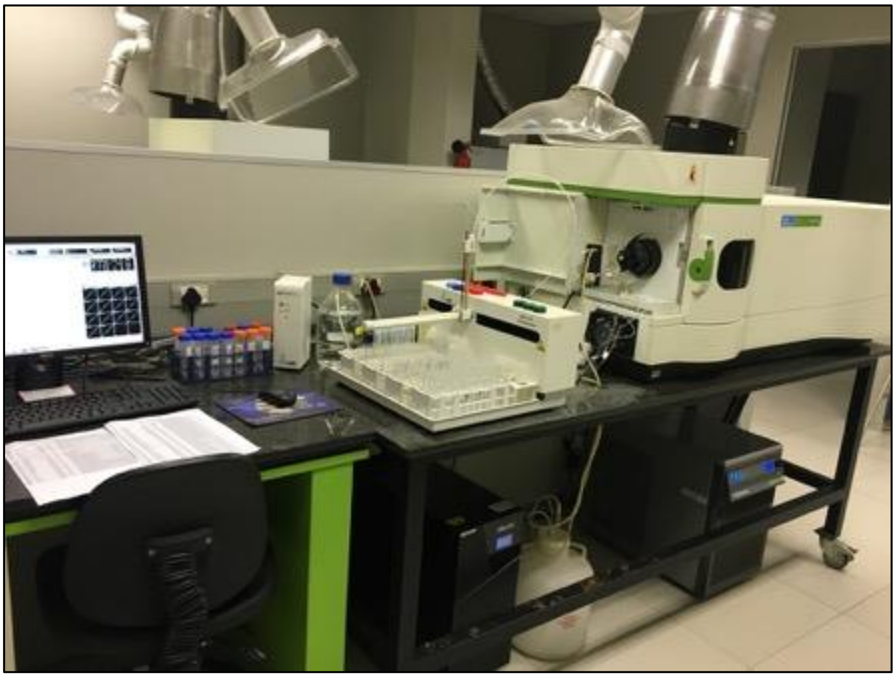


Figure 33: ICP-OES used for analysis.

3.3.4. Potentiometric determination of pH and EC

Potentiometric methods are based on measuring the potential of electrochemical cells without drawing significant current in the sample. Electrical conductivity is one of the simplest examples of potentiometric analysis since it is the measure of flow of electrical current through water. This is possible because the charge on ions dissolved in water facilitate the electrical current and therefore, the EC is proportional to the ion concentration in the sample. Two plates, usually platinum, are placed in the sample, a potential is applied across the plates and the current is measured.

The measurement of pH is more complicated and **Figure 34** shows a simplified cell for potentiometric analysis. This cell can be represented as (Skoog et al., 2004):

$$reference\ electrode(E_{ref})|salt\ bridge(E_j)|analyte\ solution|indicatorelectrode(E_{ind})$$

The reference electrode, (E_{ref}) is a half-cell with an accurately known electrode potential that is independent of the concentration of the analyte or any other ions in the sample. The indicator electrode (E_{ind}) is in the sample and develops a potential that is proportional to the activity of the sample. The salt bridge (E_j), which is the third component of a potentiometric cell, prevents the component of the analyte solution from mixing with the reference electrode. A potential develops across the liquid junction at each end of the salt bridge. These two potentials need to cancel each other out and to achieve that potassium chloride is used as the salt bridge because the mobility of K^+ and Cl^- are nearly equal resulting in a very small E_j.

The results are calculated by the following **Equation 4**:

$$\boldsymbol{E_{cell} = E_{ind} - E_{ref} + E_j} \qquad \textbf{\textit{Eq. 11}}$$

The concentration of the analyte is E_{ind}.

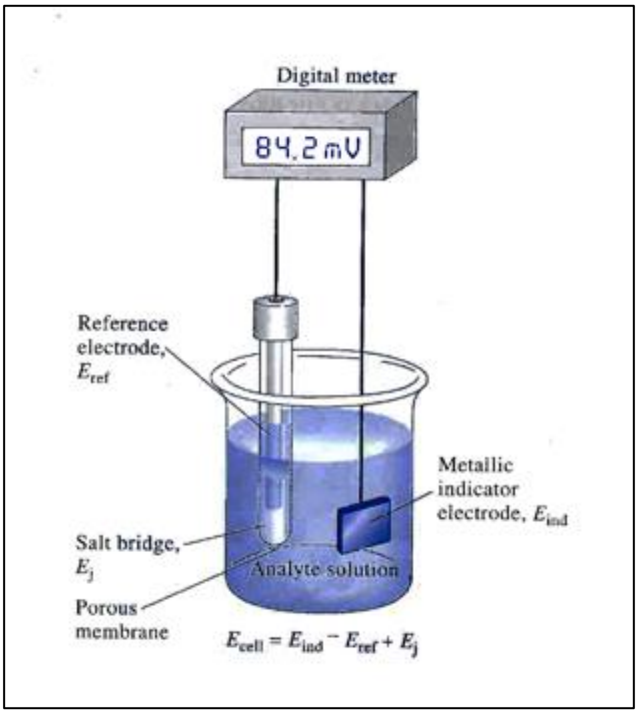
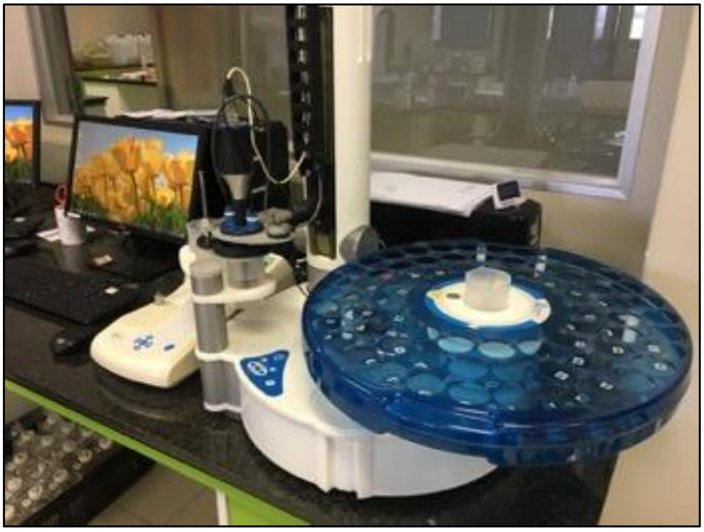


Figure 34: A cell for potentiometric determination (Skoog, 2004).

pH and EC were measured simultaneously with an auto sampler as seen in **Figure 35(a)** that introduces the pH and EC probes into the sample to obtain the measurement. The pH for the samples was measured with a Red Rod pH probe seen in **Figure 35(b).** This probe consists of a glass indicator electrode with an internal reference electrode of silver/silver chloride (Ag/AgCl) and a liquid junction of potassium chloride.

The EC for the samples was measured with a Mode d'Emploi 2-pole conductivity cell displayed in **Figure 35(c)**.



(a) Auto sampler used for pH and EC.

(b) pH probe

(c) EC probe

Figure 35: (a) Auto sampler where the sample was poured into cups and placed in a rotating base so that the(b) pH probe and (c) EC probes can be lowered into the sample for the analyses to take place.

3.3.5. Total Dissolved Solids (TDS)

To determine the TDS the suspended solids first need to be removed by filtering the water sample through a 2 μm glass filter as seen in **Figure 36(a)**. TDS is then determined by a gravimetric method. A glass dish is pre-weighed and then the sample is evaporated to dryness in the pre-weighed glass dish seen in **Figure 36(b)**. After evaporation, the dish is also dried in an oven at 180 °C and then a post-weight is taken of the dish. The difference between the pre-weighed and post-weighed dish is equal to the TDS in the sample (APHA, 2005).

(a) Filtration unit used for TDS.

(b)Evaporation unit used for TDS.

Figure 36: TDS evaporation and filtration stand.

3.3.6. Stable isotopes

The Los Gatos Research DLT -100 (LGR DLT-100) is used to measure stable isotopes in liquid water samples **(Figure 37)**. This instrument measures laser absorption within a highly reflective-mirror cavity. This cavity with mirrors creates path lengths of several kilometres resulting in a difference in laser absorption lines for different water molecules. This method is called Wavelength-Scanned Cavity Ring Down Spectroscopy (IAEA, 2009).

All the samples were analysed with this instrument at iThemba Labs in Johannesburg for stable isotopes and the measurement of uncertainty is reported in **Table 6**.

Table 6: Measurement of Uncertainty for the stable isotopes.

Analyte	Uncertainty of Measurement (%)
Oxygen	0.5
Hydrogen	1.5

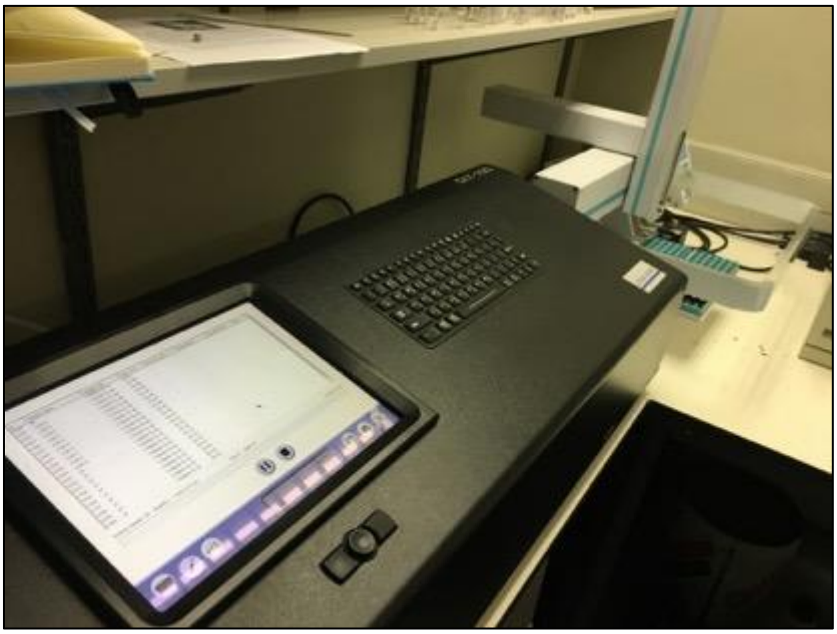


Figure 37: Los Gatos Research DLT-100.

3.3.7. Data acquired

Older historic data was also acquired from Aquatico since they have been involved with PPC Mooiplaas groundwater monitoring since 2013. The sampling points they sample monthly is the groundwater (GWF1, GWF12 and GWF2). Other locations they sample on a quarterly basis include the two pit lakes, the fish dam, the Hennops River and several drinking waterpoints on the site.

3.3.8. Data validation

The samples were analysed each month and each month a blank sample was included to assess the quality of the analysis. Thus, in total there were six blank samples. The blank sample is only relevant to the inorganic chemistry analysis. The blank sample values were evaluated by comparing it to the minimum and maximum values of the rainwater values. For example, the EC for these six blank samples was compared to the EC values of the rain samples. The EC for the rain samples ranged from 1.79 mS/m to 4.60 mS/m and the EC values for the blank samples ranged from 0.31 mS/m to 1.52 mS/m, and since the EC values for the blank samples were lower than that of the EC values for the rainwater it indicates good quality analysis for the chemistry results. The comparison of the rain water to the blank sample values of all the parameters analysed for can be seen in **Table** 10 of **Appendix B**.

Duplicate samples were also included during the sampling period for both the inorganic chemistry and isotope analyses to check if the analyses were precise. Since the results for the duplicate samples should be very similar, the relative percent difference (RPD) was used to measure the precision between the duplicates. The RPD was calculated for each duplicate sample with **Equation 12** and for a good water analysis the RPD should be less than 10%. The evaluation of the inorganic analysis duplicate samples are presented in **Table** 11 of **Appendix B** and from this table it is clear that 80% of the RPD values are less than 10% with only 20% of the RPD values above 10%. The evaluation of the isotope duplicates analyses is presented in **Table 12** of **Appendix B** and all of the RPD values calculated were below 10% for the isotope duplicates.

$$\boldsymbol{RPD = \frac{a-|b|}{a+b} \times 100} \qquad \textbf{\textit{Eq. 12}}$$

The charge balance of all the inorganic chemistry analyses was also checked by using a program called PHREEQC. This program calculates the RPD between the sum of the cations to the sum of the anions. Since the sum of the cations and the sum of the anions should be equal to each other (Apollo and Postma, 2005), RPD was also used to measure the difference between the sum of anions, and the sum of cations, and for a good water analysis the RPD should be less than 10%. The RPD values for all the water quality data obtained during this study is presented in **Table 13** and **Table 14** of **Appendix B.**

The laboratory results were assessed with these three principles and were found to be acceptable for the purposes of this assessment.

4. Results

4.1. Chemistry results

The average values for each of the sampling locations are presented in **Table 7**. The statistical analysis of physicochemical parameters of all the chemistry data are summarised in **Table 15** to **Table 21** in **Appendix C**. The test reports for the chemistry analysis is in **Appendix D**. The concentration of NH_4^+, K^+ and Na^+ are lower than that of Mg^{2+} and Ca^{2+} therefore, the relative abundance of the major cation's concentrations is $Ca^{2+}>Mg^{2+}>Na^+>K^+>NH_4^+$. The Ca^{2+} concentrations range from 0.82 mg/L to 139 mg/L, the Mg^{2+} concentrations range from 0.077 mg/L to 77.7 mg/L, the Na^+ concentrations range from 0.18 mg/L to 166 mg/L, the K^+ concentrations range from 0.02 mg/L to 28.5 mg/L and the NH_4^+ concentrations range from 0.008 mg/L to 28.1 mg/L. With respect to major anions the relative abundance is: $SO_4^{2-}>Cl^->NO_3^->PO_4^{3-}>F^->Br^-$ and the concentrations ranged from 0.141 mg/L to 122.00 mg/L for SO_4^{2-}, 0.86 mg/L to 205.00 mg/L for Cl^-, 0.194 mg/L to 29.3 mg/L for NO_3^-, 0.005 mg/L to 13.7 mg/L for PO_4^{3-}, 0.263 mg/L to 1.67 mg/L for F^- and 0.01 mg/L to 0.86 mg/L for Br^-.

Figure 38 presents a Piper diagram for all samples in this study. The chemical signature of the samples is mainly Ca^{2+}-Mg^{2+}-HCO_3^- with a slight trend to SO_4^{2-} and Cl^-, which suggests carbonate mineral dissolution. This is consistent with the dolomite environment of the study area. The bulk of the samples are in the Ca^{2+}-HCO_3^- facies with the two exploration boreholes in the furthest left-hand corner of the central diamond indicating freshly recharged groundwater. There are also three other groups on the central diamond which include the Hennops River upstream (HR Us) and Hennops River downstream (HR Ds) samples which are mixed Ca^{2+}-Na^+-HCO_3^- facies. The sump samples plot as a separate field but is still part of the Ca^{2+}-HCO_3^- facies. The rain samples plot as part of the Ca^{2+}-Cl^- facies.

Thus, from the Piper diagram four different groupings of water can be seen in the study area (**Figure 38**). The first is the HR which is in the middle of the diamond, the second is the Sump water just left of the HR water, the third is rain samples to the top right corner, and then lastly all the rest of the sampling locations at the mine that plot in one area on the left hand boarder of the central diamond.

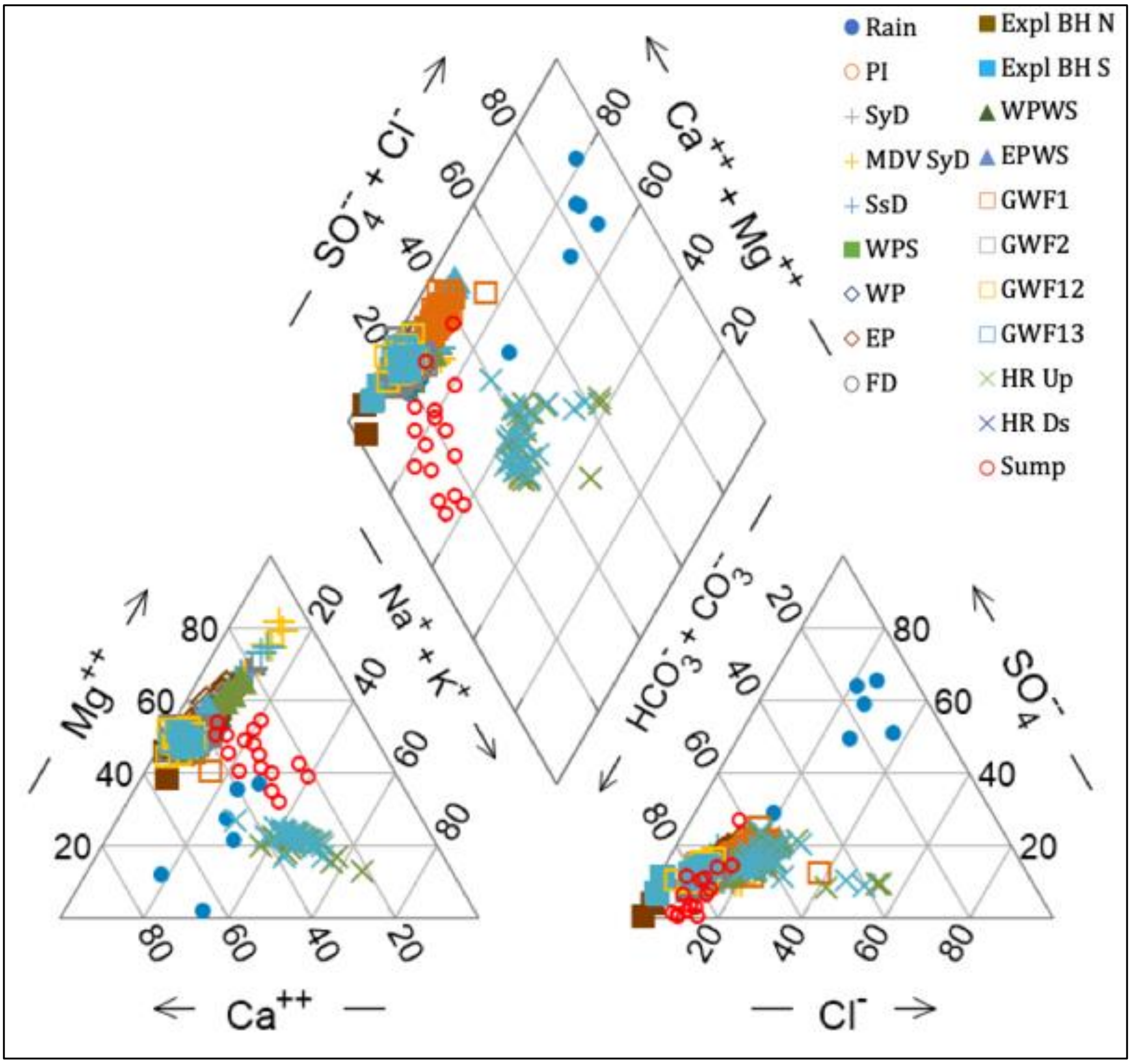


Figure 38: Piper diagram of water quality according to different sampling locations sampled from April 2017 to September 2017 and the historic data obtained from Aquatica from January 2013 to October 2017.

In **Figure 39** box and whisker plots are presented for pH and Electrical Conductivity (EC) to evaluate the relationship between the different sampling locations and from these plots further groupings can be seen. The pH of the water is generally alkaline, with average values ranging from 7.25 to 9.02 except for the rainwater samples with pH average value of 6.18. The groundwater samples (GWF12, GWF13, GWF1, Expl BH N and Expl BH S) all have pH average values lower than the surface water samples (PI, WP, EP, FD, SyD, MDV SyD, SsD, WPWS, EPWS, WPS) form the mine and the Hennops River.

The EC box and whisker plots shows that the Groundwater Flow 1 (GWF1), West Pit Wall Seep (WPWS) and East Pit Wall Seep (EPWS) having higher than normal values, and the Exploration Boreholes (Expl BH N and Expl BH S) have lower than normal values and then the majority of the water from the mining activity in between these extremes. The Hennops river samples and the Sump samples have similar EC values to the majority of the water at PPC Mooiplaas.

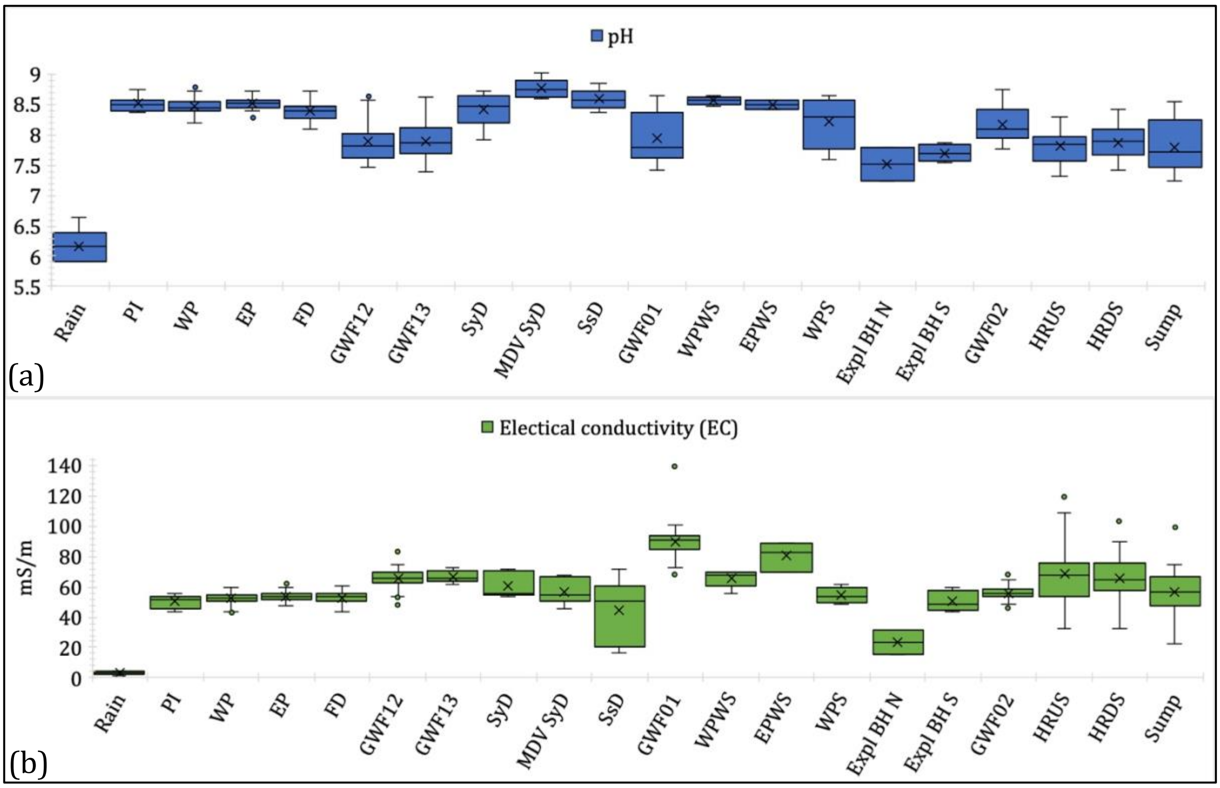


Figure 39: Box and whisker plots showing distribution of data for (a) pH and (b) EC in relation to the other sampling locations.

NH_4^+ and NO_3^- are plotted against each other in **Figure 40** to illustrate the abundance of NO_3^- in the mining samples and the lack thereof in the Hennops River. The opposite is true with regards to the NH_4^+; it is abundant in the Hennops River but not in the mining samples. NO_3^- in the mining related samples is between 7 mg/L and 13 mg/L but in the Hennops River the range of concentrations are 1.47 mg/L to 2.09 mg/L. With regards to NH_4^+ the mining samples contain 0.08 mg/L to 2.06 mg/L of NH_4^+ and the Hennops River contains between 9.09 mg/L and 10.2 mg/L. It is also interesting to see that the exploration boreholes have very little NO_3^- (average: 0.64 mg/L) but a significant amount of NH_4^+ (average: 4.79 mg/L).

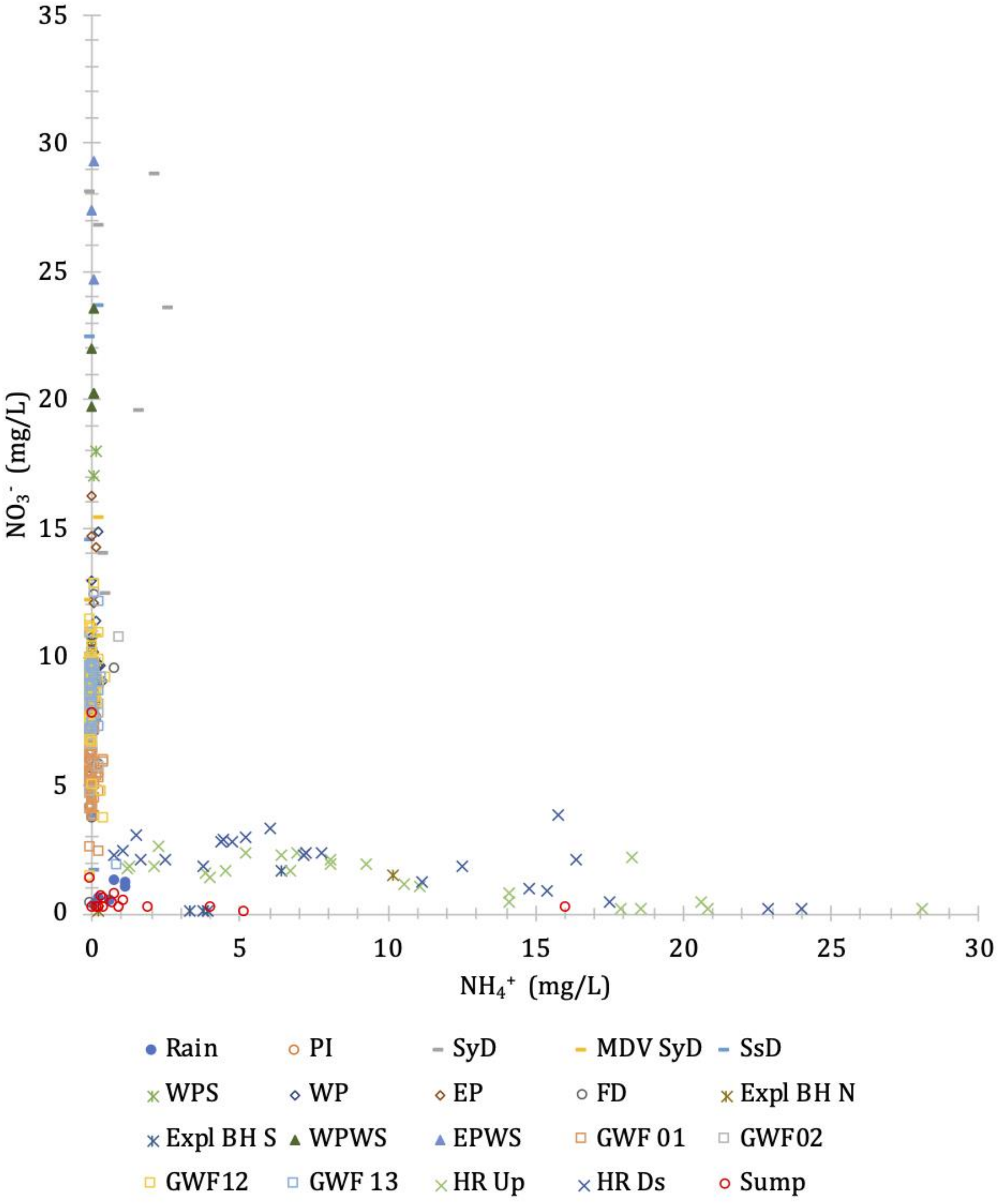


Figure 40: Scatter plot for NH_4^+ vs. NO_3^- indicating the difference between Hennops river samples and the mining samples.

In **Figure 41**, the NO_3^- plotted against Cl^- to illustrate the different amounts of NO_3^- in the sampling locations. From this scatter plot it is seen that the NO_3^- in the Slurry Dam (SyD), Slimes Dam (SsD) and Wall Seeps (WPWS and EPWS) are the highest (average: 20 mg/L), with all the other sampling locations related to the mine with NO_3^- values between 7 mg/L and 13 mg/L. Closer to the Hennops river it is also seen that groundwater has high values of NO_3^- since it is also found in the Groundwater Flow 2 (GWF2) borehole (average: 8.53 mg/L) even though GWF2 is located more than one kilometre downstream of the mine, just north of the Hennops River. The Hennops River also contains NO_3^- (average: 1.78 mg/L), but to a much smaller extent. On the other end of the spectrum this plot also shows that the Exploration boreholes (Expl BH N and Expl BH S) have almost no nitrates in it. This plot also shows that even though Groundwater Flow 1 (GWF1) also contain similar amounts of NO_3^- as the other mining samples it does form a different cluster with higher amount of Cl^- than the rest of the groundwater samples.

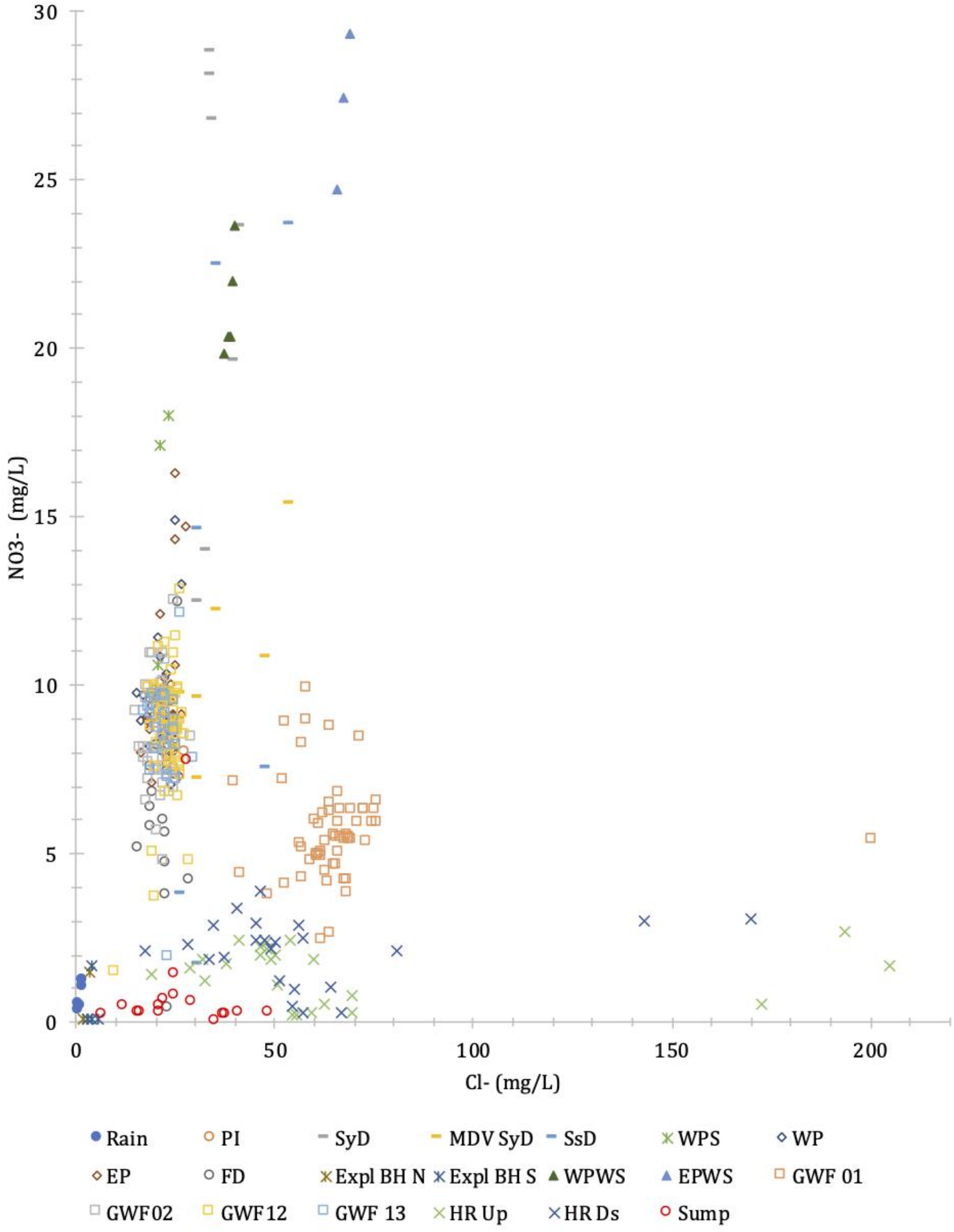


Figure 41: Scatter plot for Cl^- vs. NO_3^- showing different concentrations of nitrate in the different sampling locations.

Figure 42 is a scatter plot of Mg^{2+} vs SO_4^{2-} and in this figure the difference of GWF1 is also clear showing that it has a different dissolved inorganic mineral content than the rest of the sampling locations. It was also clear that with the mining samples' clear clusters formed with the dominant three pointed out in **Figure 42**. The cluster labelled 1 is the majority of the surface water which is the Fish Dam (FD), East Pit (EP), West Pit (WP) and then also the Plant Inlet (PI). The cluster labelled 2 is groundwater from the two boreholes within the quarry known as GWF12 and GWF13 and then lastly the cluster labelled 3 is groundwater from the borehole GWF1. The Slimes Dam (SsD), Slurry Dam (SyD) and the MDV Slurry Dam (MDV SyD) also have a different chemical signature than the rest of the mining samples as it deviates from the clusters as outlined and ladled with number four in **Figure** 42. From the same figure it is also seen that the WPWS in circled five plots close to the SsD, SyD and MDV SyD and then in strong contrast the EPWS plots well within the field for the borehole GWF1 circled with number six. These different clusters are seen throughout the different parameters analyses for with some plots showing the clusters better than others.

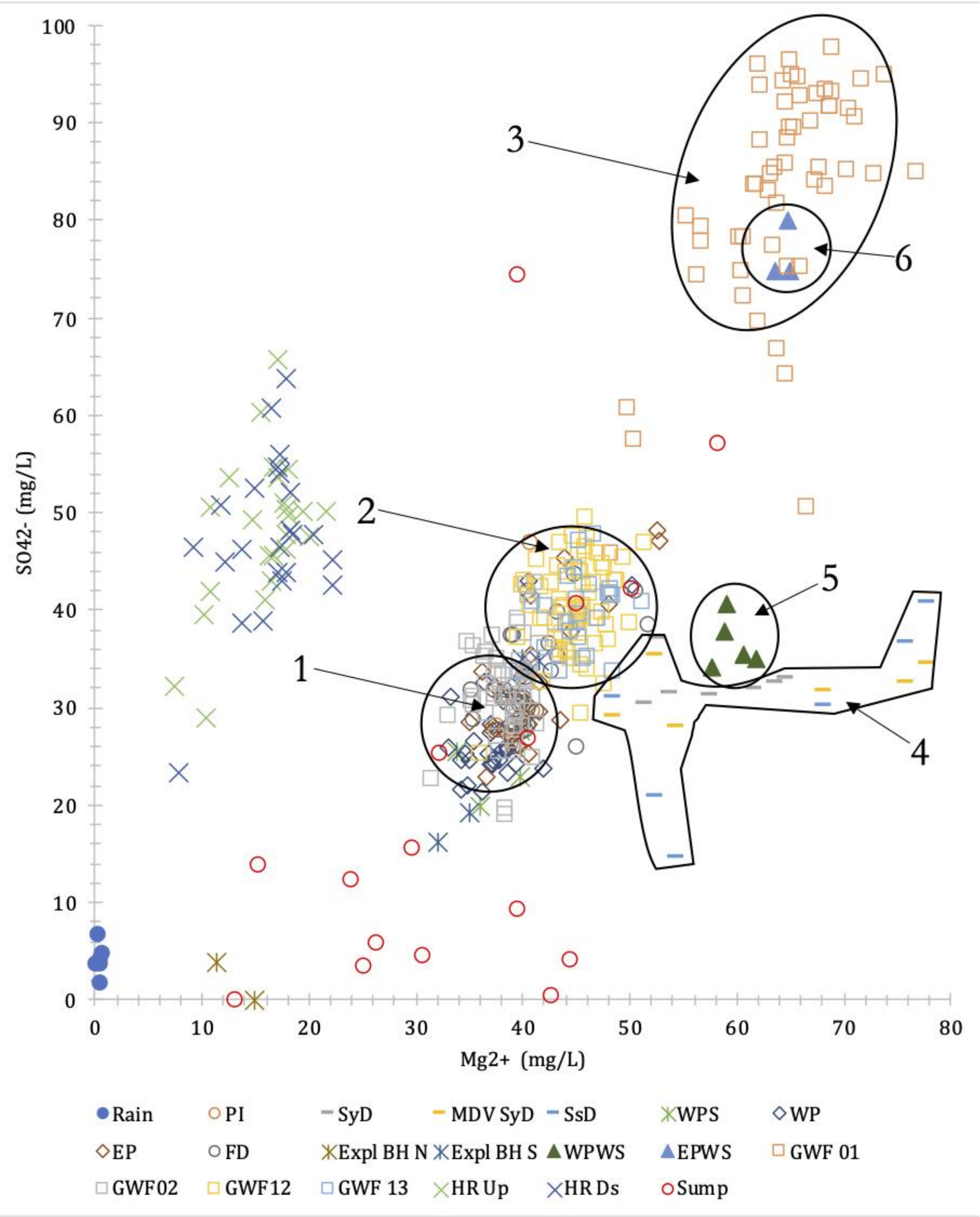


Figure 42: Scatter plot for Mg^{2+} vs. SO_4^{2-} for all samples and data obtained indicating three clusters formed by the mining samples. This plot also shows the and the deviation of the SsD, SyD and MDV SyD outlined and ladled by number four. With circle number 5 it is shown that the WPWS plots alongside the SsD, SyD and MDV SyD. Then lastly it is important to note that the EPWS plots with GWF1 as indicated in circle six.

Table 7: Average values of chemical paraments per sampling location.

Parameter	Unit	Average water quality of sampling locations																			
		Rain	PI	WP	EP	FD	GWF 12	GWF 13	SyD	MDV SyD	SsD	GWF 1	WP WS	EPW S	WPS	Expl BH N	Expl BH S	GWF 2	HRU S	HRD S	Sump
	n	6	7	29	29	30	62	24	7	6	6	57	5	3	4	2	4	59	24	23	16
pH	-	6.18	8.52	8.47	8.52	8.39	7.91	7.90	8.43	8.77	8.59	7.94	8.57	8.49	8.22	7.52	7.70	8.18	7.82	7.87	7.81
EC	mS/m	3.20	50.5	52.3	53.4	53.0	65.7	67.2	61.0	57.1	44.7	89.9	65.4	80.5	54.5	23.5	50.2	56.1	69.1	66.1	56.1
TH	mg $CaCO_3$/L	14.2	322	306	307	308	83.1	376	401	359	289	546	433	552	341	154	307	326	381	364	317
Alkalinity	mg $CaCO_3$/L	1.62	212	203	198	207	263	263	205	225	162	319	229	226	211	153	276	219	199	193	247.5
Cl^-	mg/L	1.52	23.6	21.4	22.7	22.8	23.7	22.7	35.4	37.8	26.1	66.2	38.8	67.3	21.9	2.69	4.16	21.9	66.2	57.9	26.5
SO_4^{2-}	mg/L	4.18	31.8	27.4	32.5	32.5	40.5	39.9	32.7	32.0	29.2	84.6	36.7	76.7	24.1	2.01	26.4	32.4	48.1	47.6	21.1
NO_3^--N	mg/L	0.79	8.64	9.75	9.74	7.48	8.67	8.49	21.9	10.8	12.3	5.65	21.2	27.1	13.9	0.79	0.49	8.53	1.47	2.09	0.86
NH_4^+-N	mg/L	0.74	0.09	0.11	0.06	0.10	0.10	0.15	1.10	0.13	0.37	0.09	0.04	0.04	0.08	5.21	4.37	0.08	10.2	9.08	2.06
PO_4^{3-}-P	mg/L	0.07	0.05	0.03	0.03	0.09	0.03	0.03	0.04	0.05	0.03	0.05	0.03	0.04	0.02	0.56	0.03	0.03	1.21	0.97	3.28
F^-	mg/L	0.15	0.18	0.21	0.20	0.21	0.21	0.23	0.19	0.21	0.23	0.24	0.13	0.13	0.16	0.24	0.27	0.20	0.25	0.26	0.46
Ca^{2+}	mg/L	1.89	45.2	48.2	44.6	44.2	70.4	69.9	32.2	19.6	20.9	91.5	45.8	70.9	53.7	28.6	57.3	55.4	38.7	39.2	38.8
Mg^{2+}	mg/L	0.41	39.3	37.5	40.9	40.9	44.9	45.5	57.8	62.8	44.4	64.3	59.6	64.4	37.3	13.1	37.2	38.9	15.7	16.8	34.8
Na^+	mg/L	0.71	13.1	12.2	12.2	12.4	9.85	9.93	16.8	17.6	12.0	19.3	17.6	14.9	13.7	1.08	2.83	10.6	64.7	58.7	30.1
K^+	mg/L	0.67	0.71	0.60	0.73	0.74	0.88	1.35	2.50	3.16	2.04	1.05	1.18	0.20	0.55	3.14	2.67	0.55	10.2	9.75	10.1

4.1. Hydrogen and oxygen isotopes

The test reports for the isotope analysis in **Appendix E**. In this study δ^2H varied from -72.6 ‰ to 40.2 ‰ with an average value of -16.4 ‰. The δ^{18}O varied from -9.9 ‰ and 3.5 ‰ with an average of -2.9 ‰. δ^2H and δ^{18}O of the samples were plotted against each other in **Figure 43** along with the Global Meteoric Water Line (Craig 1961) and the Pretoria Meteoric Water Line from Meyer (2014) (PMWL). In addition, the Local Meteoric Water Line (LMWL) was calculated by linear regression and resulted in the red dotted line in **Figure 43.** The LMWL can be represented by **Equation 13**.

$$\delta^2H=8.07\delta^{18}O+12.51 \qquad \text{Eq. 13}$$

The LMWL in the study area is similar to the GMWL and the PMWL. The results form a cluster for δ^2H between -19.7 ‰ and -14.2 ‰ and for δ^{18}O between -3.61 ‰ and -2.25 ‰. It is also clear that there is an evaporation trendline and this is indicated with a thick purple line in **Figure 43**. The West Pit Seep (WPS) is at the lower end of the cluster and the SyD at the higher end of the cluster with GWF12, GWF1, WPWS, FD, EP, WP and the MDV SyD as the main cluster in the middle of the two extremes. The EPWS is more positive than the main cluster and the SsD is even more positive than the EPWS deviating the most from the LMWL. The two Expl BH's are more negative than the cluster.

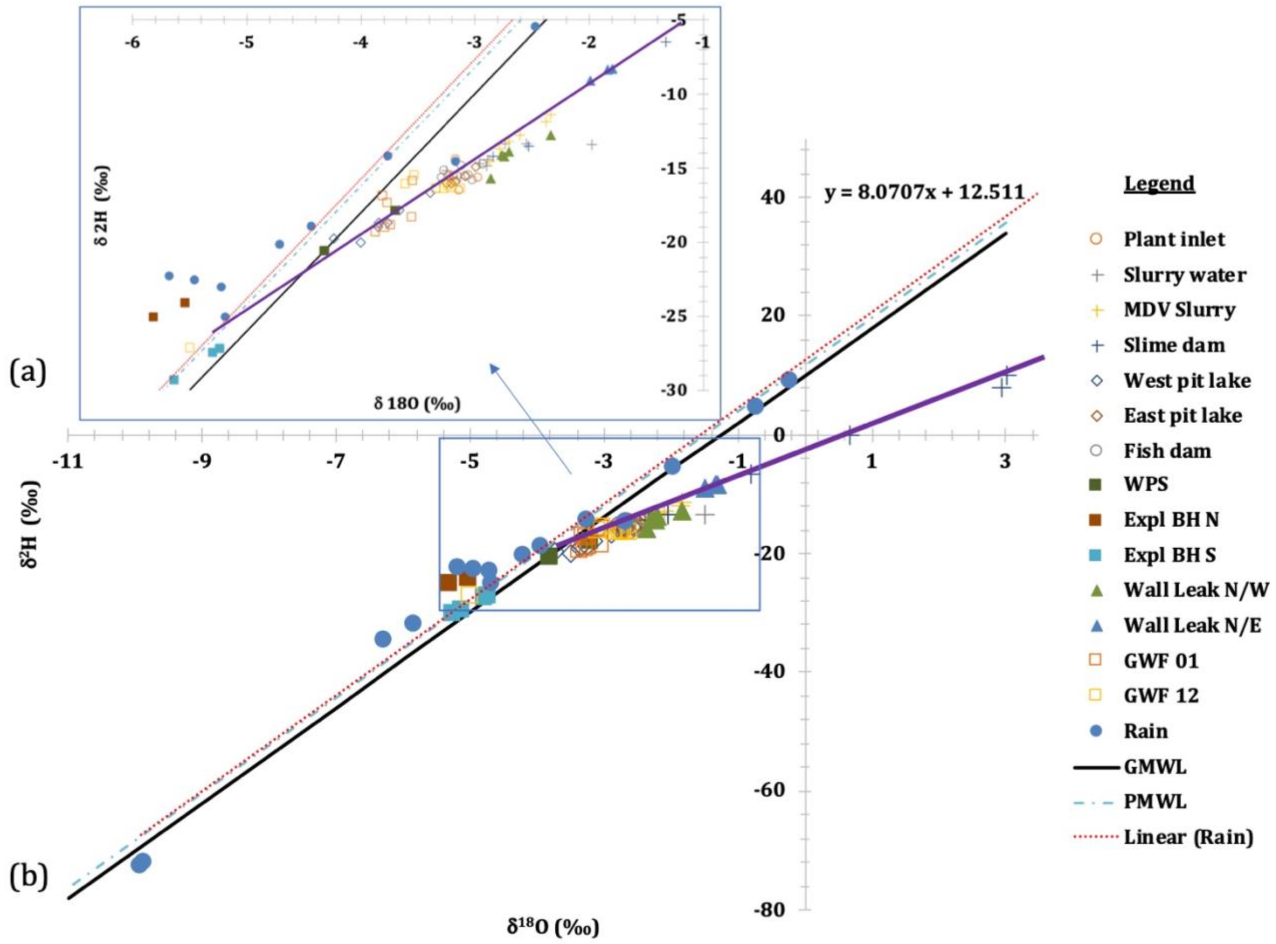


Figure 43: δ^{18}O vs. δ^{2}H of samples relative to the global meteoric water line as solid black (GMWL - δ^{2}H=8δ^{18}O+10) (Craig 1961) and the long-term Pretoria meteoric water line as a dashed blue line (PMWL - δ^{2}H=8δ^{18}O+11.8) (Meyer 2014). The Local Meteoric Water Line (LMWL - y = 8.0707x + 12.511) was calculated by linear regression and resulted in the red dotted line. The evaporation trendline indicated in purple.

5. Discussion

5.1. Hydrogeochemical characterisation of PPC Mooiplaas

The piper diagram in **Figure 38** show that the water chemistry type in the study area for all the mining samples is Ca^{2+}-Mg^{2+}-HCO_3^- with a slight trend to SO_4^{2-} and Cl^-. This is consistent with a karstic or dolomitic environment found across the world (Dişli, 2019; Gu et al., 2017; Yuan et al., 2017; Williams, 2007) and in South Africa (Meyer, 2014; Holland & Witthüser, 2008; Hobbs and Cobbing, 2007; Mndaweni et al., 2019). The fact that the groundwater plot in the left-hand corner of the piper diagram indicate freshly recharged groundwater.

In the box and whisker plot of pH in **Figure 39(a)** it is also seen that the groundwater (GWF12, GWF13, GWF1, Expl BHN and Expl BHS) has lover pH values than the surrounding surface water bodies in the study area. This is also be a contribution of freshly recharged groundwater as its clearly seen the pH of the rainwater is much lower that the PPC Mooiplaas sampling locations.

In **Figure 39(b)** it is seen that the GWF1 and EPWS both have higher than normal EC values. This is due to the close proximity both these sampling locations have to the dykes cross cutting the study area. The different geological unit is resulting in a different water chemistry in these two samples.

The HR shows a completely different water chemistry as opposed to PPC Mooiplaas in the Piper diagram (**Figure 38**). The chemistry of the HR and PPC Mooiplaas is especially different with regards to NH_4^+ and NO_3^-, as seen in **Figure 40**. From the chemistry results, it is quite clear that groundwater does move from the PPC Mooiplaas' down gradient to the HR, because GWF2, which is 1.2 km down gradient from PPC Mooiplaas and just 0.4 km north of the HR, contains almost the same amount of NO_3^- (average NO_3^-=8.53 mg/L) than the majority of the water samples at PPC Mooiplaas (average NO_3^-=12.74 mg/L). However, the NO_3^- concentration drops significantly when it enters the HR (average NO_3=1.78 mg/L). This is likely due to dilution and therefore, the impact that the mine has on the HR is minimal. The main purpose of **Figure 40** is to show the different sources of anthropogenic impacts taking place in the area. The first is the ammonium which is due to sewage entering the river system from the highly populated cities e.g. Pretoria. The second is the impact the mine has on the area and that is introducing nitrates into the system due to the explosives used to extract the dolomite.

The Sump is an area that is used to wash and clean mining equipment, such as the trucks used to move the dolomite. This washing process causes oil to get into the water and because of this the mine constructed a sump where water is cleaned by a Drizit, which separates the oils from the water. The chemistry results for the Sump are from the water after it has been cleaned by the Drizit. The source of the water that is used to wash the mining equipment is unknown, however, since the Sump water also has a different chemical signature from that of the other PPC Mooiplaas water samples and that of the HR it is most probably due to a different water source e.g. municipal water. This water is then either discarded from the mine or placed back into circulation, but it is currently unknown where this water moves to after it has been cleaned by the Drizit.

5.2. Comparing PPC water chemistry to that of the surrounding karst aquifer

In **Figure 44** the piper diagram with the data obtained at PPC Mooiplaas is next to a piper diagram from Meyer (2014) with groundwater data from quaternary catchment A21B. Since PPC Mooiplaas is also in quaternary catchment A21B this is a suitable comparison. From these two Piper diagrams it is clear that there is a similar trend from Ca^{2+}-Mg^{2+}-HCO_3^- to SO_4^{2-} and Cl^-, indicating that the water at PPC Mooiplaas corresponds well with the surrounding groundwater. The Hennops River (HR) and the Sump data form different clusters on the Piper diagram which is different from the groundwater at PPC Mooiplaas and the surrounding karst environment. The Expl BHs in the left-hand corner of the diamond represent water not impacted by anthropogenic sources and the more water is influenced by anthropogenic activity such as sewage or the mine the samples will start plotting further away from the left-hand corner. As seen in **Figure 44** the more interaction the water has with the mine a trend form Ca^{2+}-Mg^{2+}-HCO_3^- to SO_4^{2-} and Cl^- is seen indicated higher concentrations of dissolved salts and as seen from the Hennops River that is contaminated by sewage the water samples will plot towards the right corner. This is consistant with what is seen in Meyer (2014).

To further understand how the water chemistry results at PPC Mooiplaas differs from the surrounding region, the average water quality of all the sampling locations at PPC Mooiplaas was compared to the minimum and maximum values for dissolved ions of the regional groundwater compartment (Alwynkop, Laudium, Fountains West and Fountains East) taken from Meyer (2014) in **Table 8.** In **Table 8** the red indicates that the average value of the specific sampling location is more than the maximum of the regional groundwater, the green indicates that the average value of the sampling location is lower than the minimum regional groundwater quality and the yellow indicates that the average value for the sampling locations falls in between the regional minimum and maximum. From this table it is clear that the groundwater at PPC Mooiplaas is very similar to that of the regional groundwater quality. The only significant difference is that the NO_3^- concentrations are higher for almost all the sampling locations except that of the HR, Sump and Exploration Boreholes (Expl BH's). This further shows that the mine is contaminating the groundwater in the area with nitrates and that the Expl BHs are the least affected by the mine.

<table>
<tr>
<td>Data obtained from PPC Mooiplaas trending from Ca^{2+}-Mg^{2+}-HCO_3^- to SO_4^{2-} and Cl^-.</td>
<td>Data from HR in Ca^{2+}-Na^+-HCO_3^- facies.</td>
<td>Groundwater data from quaternary catchment A21B indicating similar trends as PPC Mooiplaas from Ca^{2+}-Mg^{2+}-HCO_3^- to SO_4^{2-} and Cl^- (yellow arrow) with an additional trend towards Na^+ and K^+(green arrow).</td>
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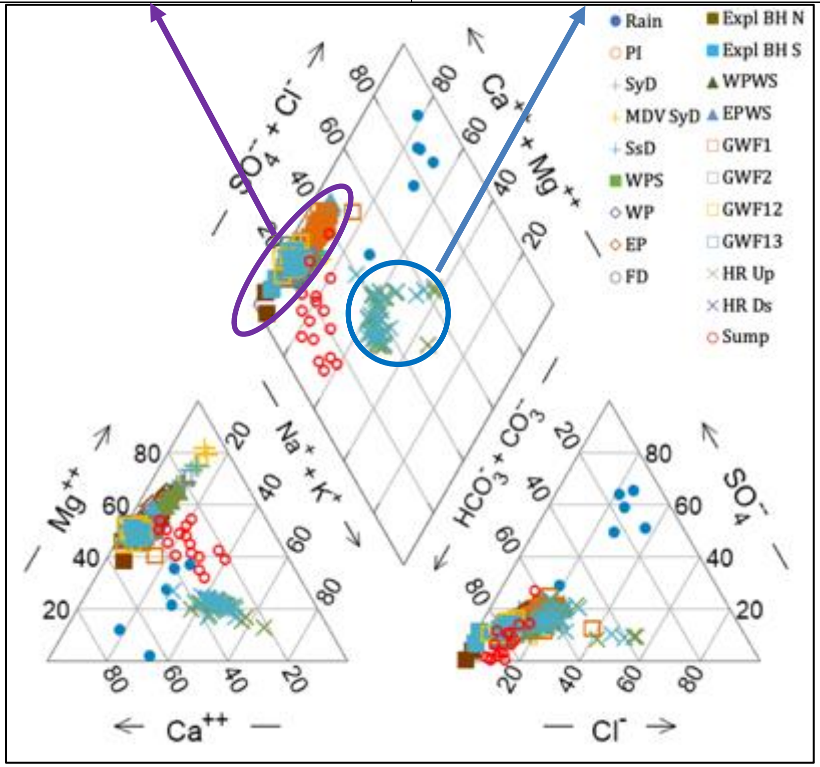
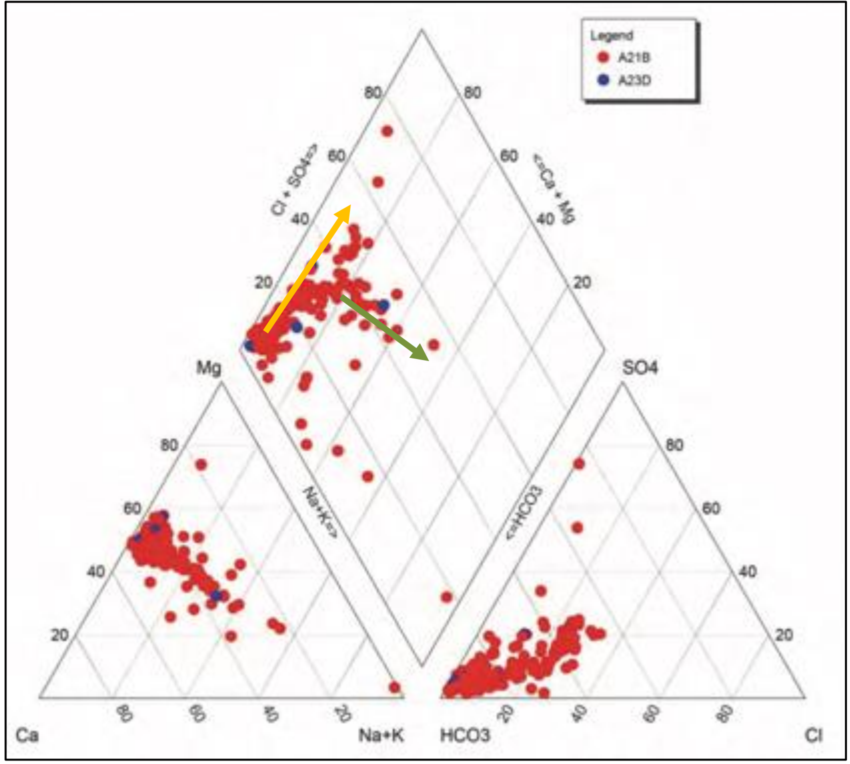
<td colspan="2">(a)</td>
<td>(b)</td>
</tr>
</table>

Figure 44: Comparison of piper diagrams (a) from chemistry data obtained at PPC Mooiplaas and (b) groundwater quality in quaternary catchment A21B and A23D from Meyer (2014). PPC Mooiplaas is located in quaternary catchment A21B making this a suitable comparison.

Table 8: Table comparing regional groundwater quality with the average water quality from all the sampling locations.

Parameter	Unit	Regional groundwater quality (Mayer, 2014)		Average water quality of sampling locations																			
		Min	Max	Rain	PI	WP	EP	FD	GWF 12	GWF 13	SyD	MDV SyD	SsD	GWF 1	WP WS	EPW S	WPS	Expl BH N	Expl BH S	GWF 2	HRU S	HRD S	Sum p
Evaluation method				Green: Below the min regional groundwater quality							Yellow: Between the min and max of the regional groundwater quality							Red: Above the max of the regional groundwater quality					
pH	-	6.35	10.0	6.18	8.52	8.47	8.52	8.39	7.91	7.90	8.43	8.77	8.59	7.94	8.57	8.49	8.22	7.52	7.70	8.18	7.82	7.87	7.81
EC	mS/m	13.7	144	3.20	50.5	52.3	53.4	53.0	65.7	67.2	61.0	57.1	44.7	89.9	65.4	80.5	54.5	23.5	50.2	56.1	69.1	66.1	56.1
TH	mg $CaCO_3$/L	95.0	1205	14.2	322	306	307	308	83.1	376	401	359	289	546	433	552	341	154	307	326	381	364	317
Alkalinity	mg $CaCO_3$/L	61.9	683	1.62	212	203	198	207	263	263	205	225	162	319	229	226	210	153	276	219	199	193	247
Cl^-	mg/L	1.50	154	1.52	23.6	21.4	22.7	22.8	23.7	22.7	35.4	37.8	26.1	66.2	38.8	67.3	21.9	2.69	4.16	21.9	66.2	57.9	26.5
SO_4^{2-}	mg/L	2.00	634	4.18	31.8	27.4	32.5	32.5	40.5	39.9	32.7	32.0	29.2	84.6	36.7	76.7	24.1	2.01	26.4	32.4	48.1	47.6	21.1
NO_3^--N	mg/L	0	4.71	0.79	8.64	9.75	9.74	7.48	8.67	8.49	21.9	10.8	12.3	5.65	21.2	27.1	13.9	0.79	0.49	8.53	1.47	2.09	0.86
NH_4^+-N	mg/L	0.02	38.3	0.74	0.09	0.11	0.06	0.10	0.10	0.15	1.10	0.13	0.37	0.09	0.04	0.04	0.08	5.21	4.37	0.08	10.2	9.08	2.06
PO_4^{3-}-P	mg/L	0	4.44	0.07	0.05	0.03	0.03	0.09	0.03	0.03	0.04	0.05	0.03	0.05	0.03	0.04	0.02	0.56	0.03	0.03	1.21	0.97	3.28
F^-	mg/L	0.05	2.20	0.15	0.18	0.21	0.20	0.21	0.21	0.23	0.19	0.21	0.23	0.24	0.13	0.13	0.16	0.24	0.27	0.20	0.25	0.26	0.46
Ca^{2+}	mg/L	0.50	162	1.89	45.2	48.2	44.6	44.2	70.4	69.9	32.2	19.6	20.9	91.5	45.8	70.9	53.7	28.6	57.3	55.4	38.7	39.2	38.8
Mg^{2+}	mg/L	1.00	102	0.41	39.3	37,5	40.9	40.9	44.9	45.5	57.8	62.8	44.4	64.3	59.6	64.4	37.3	13.1	37.2	38.9	15.7	16.8	34.8
Na^+	mg/L	1.00	121	0.71	13.1	12.2	12.2	12.4	9.85	9.93	16.8	17.6	12.0	19.3	17.6	14.9	13.7	1.08	2.83	10.6	64.7	58.7	30.1
K^+	mg/L	0.20	39.3	0.67	0.71	0.60	0.73	0.74	0.88	1.35	2.50	3.16	2.04	1.05	1.18	0.20	0.55	3.14	2.67	0.55	10.2	9.75	10.1

5.3. Movement of water

The flow diagram in **Figure 24** illustrates the pumped, natural and inferred movement of water in the study area. The purpose of this study is to understand how the water moves in the study area and how the water chemistry is influenced by the environment it is in. The Fish Dam (FD), East Pit (EP), West Pit (WP) and the Plant Inlet (PI) are connected via pumps and the water chemistry for these sampling locations all plot in the same area on as seen in the scatter plots (**Figure 41** and **Figure 42**). The scatter plot of Mg^{2+} vs. SO_4^{2-} which is part of the conceptual diagram in **Figure 45** will be used as an example. The majority of water samples that form a cluster circled as 1 in the scatter plot of Mg^{2+} vs. SO_4^{2-} (**Figure 45**), represent all the sampling locations that are connected with pumps thus the majority of the water at PPC Mooiplaas. The majority of the water is also indicated by a green background in **Figure 45** which can be defined as the PI, EP, WP and FD.

The Expl BH's have a similar chemical composition to that of the rest of PPC Mooiplaas, but the only major difference is that the NO_3^- concentrations in the Expl BH's (average NO_3^-=0.64 mg/L) are less than the other locations (average NO_3^-=12.74 mg/L). AS seen in the piper diagram this lack of nitrates further indicates that the Expl BH's are the most representative of the natural groundwater in the study area. There is also a significant difference between Expl BH N and Expl BH S since the majority of the parameters tested for are elevated for Expl BH S when compared to Expl BH N (e.g. average EC values for Expl BH N: 23.5 mS/m and for Expl BH S: 50.2 mS/m). This difference is most likely due to the fracturing that crosscuts Expl BH S but not Expl BH N (**Figure 13**). These faults are also most likely the cause of the West Pit Seep (WPS) since the chemistry of the WPS (average EC=54.5 mS/m) and the Expl BH S are more similar than Expl BH N. The concept of the fault and the EC values for the Expl BH N, Expl BH S and the WPS is illustrated in **Figure 45**. The similarities between Expl BH S and the WPS indicates that groundwater to the west of the pit moves along the fault zone towards the pit.

The cluster circled as 2 in the scatter plot of Mg^{2+} vs. SO_4^{2-} (**Figure 45**), is represented by GWF12 and GWF13 that plot together with slightly higher Mg^{2+} and slightly higher SO_4^{2-}. GWF13 is on the lowest bench in the middle of the EP and WP and GWF12 is on the bench just above GWF13 (please see **Figure 26** Sampling locations and **Figure 25** Cross section). From the chemistry it seems that the water moves through the dolomite from

GWF12 to GWF13 and from there into the EP. GWF12 and GWF13 does have a slightly different chemical signature to that of the majority water samples, which is most likely due to the close proximity to the dyke 2 or the fact that it is groundwater and not surface water.

GWF1 forms the cluster circled as 3 in the scatter plot of Mg^{2+} vs. SO_4^{2-} (**Figure 45**), with higher than normal Mg^{2+} and SO_4^{2-}. GWF1 is a borehole located 10 m east of the Slimes Dam (SsD) with an average water level of approximately 70 m. GWF1 plots very close to the rest of the water chemistry in the Piper plot (**Figure 44**) but in all the scatter plots GWF1 is different from the rest of the sampling locations. According the Mishra et al. (2004) and Saliu and Shebu (2012) dolomite mining results in elevated hardness of more than 300 mg/L. From the line diagram in **Figure 39** one can see that GWF1 has an exceptionally high total hardness therefore, the high concentration of parameters in GWF1 could be from water seeping down from the SsD and the plant which will increase the total hardness.

GWF1 is also drilled in close proximity to dyke 1, and since the exact location of dyke 1 is unknown it could also be that GWF1 is drilled into the dolerite dyke, resulting in a different water rock interaction at GWF1, explaining the different chemical compositions. The contact zone between the dolomite and the dyke could also cause preferential flow paths due to an increase in fracturing and also dolomite dissolution (Mndaweni et al., 2019).

The wall seeps were observed on the northern wall of the quarry, one east of dyke 2 and one west of dyke 2. The SsD and GWF1 are approximately 20 m north of the quarry. From the scatter plots in **Figure 41** and **Figure 42**, one can see that the East Pit Wall Seep (EPWS) plots with the GWF1 samples and the West Pit Wall Seep (WPWS) plots in between GWF1 and the Slimes Dam. The fact that the EPWS has a similar chemical composition as GWF1 suggests the two locations have something in common: Either that the EPWS is directly connected to GWF1 or that EPWS is exposed to the same water-rock interaction which will result in a similar chemical composition as GWF1. There is very little chemical change from the movement between GWF1 and the EPWS. WPWS shows a very similar chemical signature to the SsD, indicating that the water moves from the SsD through the dolomite, towards the quarry. The conceptual movement of the water can be seen in **Figure 45.**

The isotope data will be used to identify how much influence GWF1 and the SsD have on the EPWL and the WPWS.

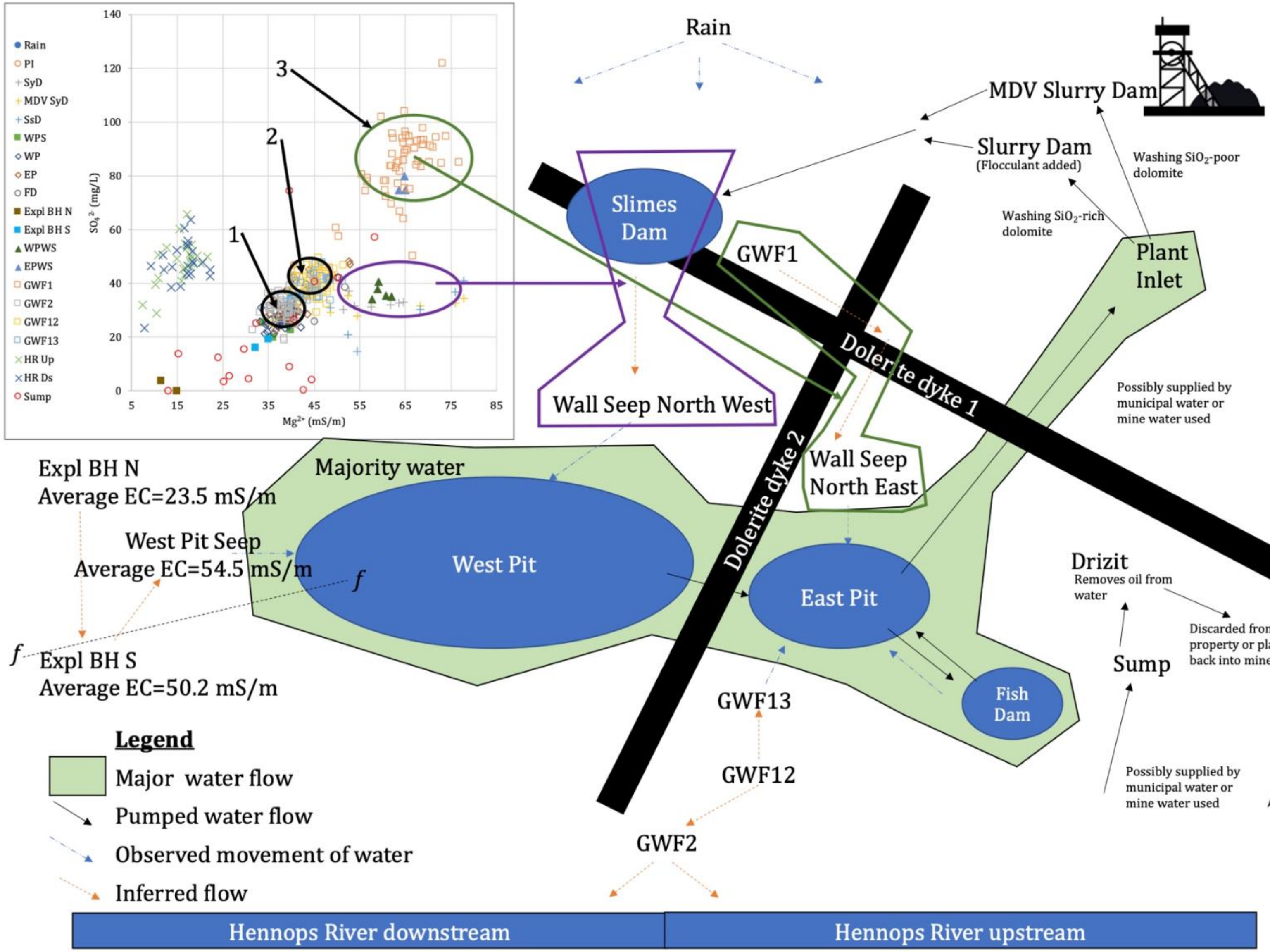


Figure 45: A conceptual diagram depicting the water movement in the study area with respect to a Mg^{2+} vs. SO_4^{2-} scatter plot.

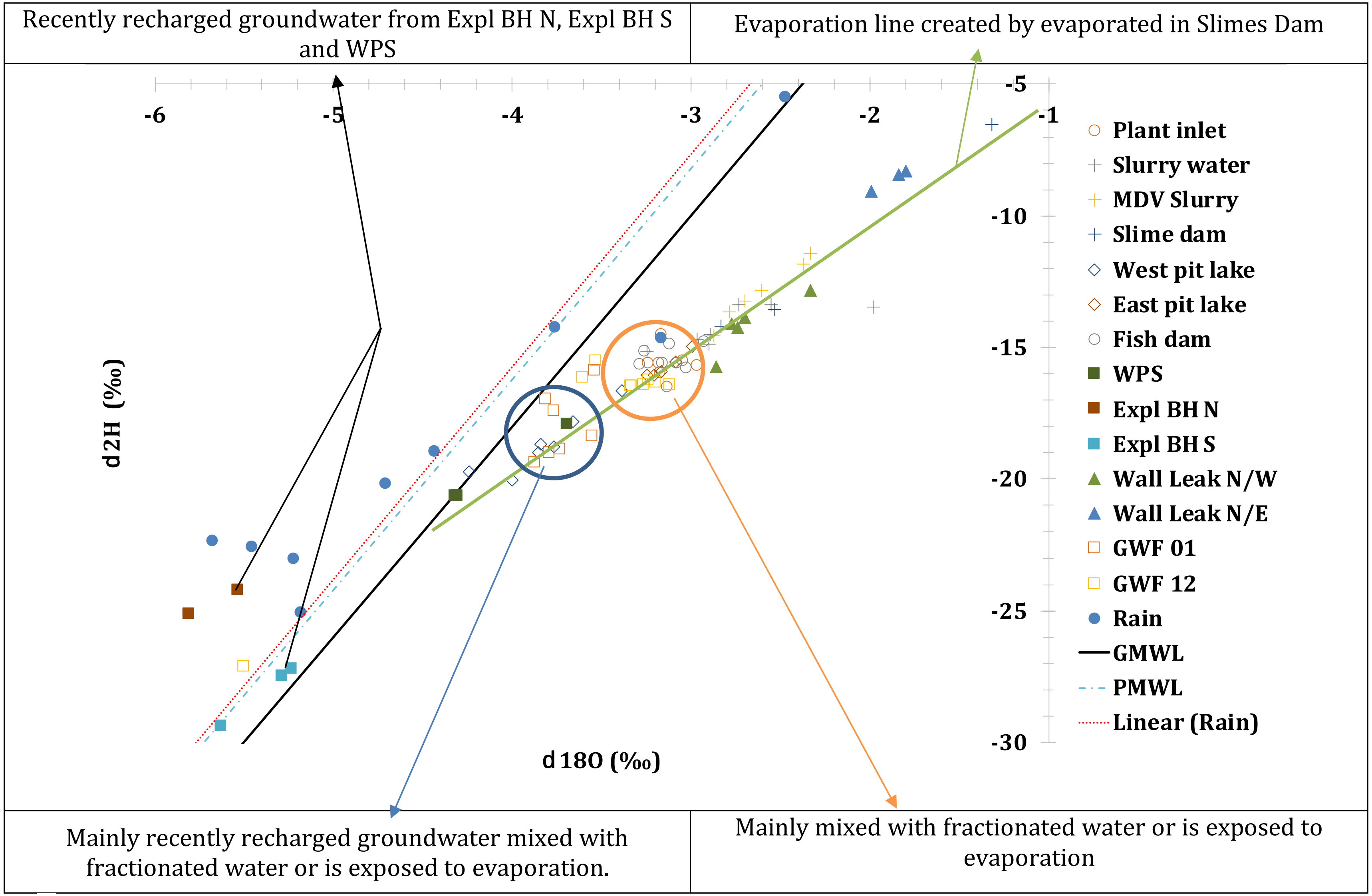
5.4. Water source

Isotope data was obtained for the rainwater near the study area to compare it to the Pretoria Meteoric Water Line (PMWL) (Meyer, 2014) and the Global Meteoric Water Line (GMWL) (Craig, 1961). From **Figure 46** it is quite clear that the rainwater from the study area does correspond to the PMWL and the GMWL. The isotope data for the rainwater was also used to calculate a Local Meteoric Water Line (LMWL) which can be represented by **Equation 13** ($\delta^2H=8.07\delta^{18}O+12.51$).

According to **Figure 6** which is adapted from Pang et al., 2017 and Coplen et al., 2000, groundwater that infiltrates quickly will have the same isotopic ratio than that of the rainfall in the area. In **Figure 46** the black lines point to the Expl BH N, Expl BH S and WPS which plots on the LMWL therefore, indicating that it is recently recharged in the same area and therefor the isotope data correlates with what is seen in the inorganic chemistry.

From **Figure 7** which was adapted from Pang et.al.,2017 and Eloy, 2004, one can see that when water is exposed to evaporation, fractionation occurs which results in the isotope ratio to deviate from the LMWL. The more the water was exposed to evaporation, the greater the deviation will occur in the isotope ration. The blue lines in **Figure 46** plot to the WP, GWF1 and GWF12 which shows a slight deviation from the LMWL thus indicating that the water in the WP is mainly groundwater exposed to evaporation, and the groundwater from GWF1 and GWF12 is slightly recharged by surface water. The orange lines in **Figure 46** indicate water that is more exposed to evaporation which is mainly the surface water located on the mine e.g. PI, EP, SyD, MDV SyD and the FD. The orange lines also indicate towards the EPWS and the WPWS which is not exposed to evaporation since the water was sampled directly from the quarry wall. Therefore, these seeps must be mixtures between groundwater and the SsD and since the WPWS is closer to the groundwater on the evaporation line it can be said that the WPWS is mainly groundwater mixed with a smaller amount of the SsD water. The EPWS plots the farthest from the groundwater indicating that the EPWS directly related to the SsD is mainly mixed with fractionated water from the SsD. Thus, the similar chemical composition of GWF1 and EPWS has more in common with the water-rock reaction along the dolerite dyke than GWF1 being the source of the water emanating at EPWS.

The main purpose of the isotope analysis was to identify if the water from the seeps water is groundwater or if it is water seeping through the vadose sone from the SsD. The isotope data shows that the EPWS does originate from the SsD and the WPWS also originate from the SsD but with a larger component of groundwater.



Recently recharged groundwater from Expl BH N, Expl BH S and WPS

Evaporation line created by evaporated in Slimes Dam

Mainly recently recharged groundwater mixed with fractionated water or is exposed to evaporation.

Mainly mixed with fractionated water or is exposed to evaporation

Figure 46: δ^{18}O vs. δ^{2}H of all samples relative to the Global Meteoric Water Line (GMWL) (Craig 1961) and long-term Pretoria Meteoric Water Line (PMWL) (Meyer 2014) as well as the calculated Local Meteoric Water Line (LMWL). This figure also indicates the evaporation line created by the Slimes Dam.

5.5. Anthropogenic impacts on karst aquifer

The anthropogenic impact the mine has on the karst aquifer is related to groundwater quality deterioration as a result of NO_3^- that is introduced as a result of blasting. This is seen by the high values in all the surface water mining samples (EP, WP, PI, SsD etc.), groundwater samples around the mine (GWF1 and GWF12) and downstream of the mine (GWF2). There was no NO_3^- found in the Expl BHs to the west of the quarry therefor the groundwater flow direction is expected to be directly south towards the Hennops River.

NO_3^- values of more than 10 mg/L can cause serious health risk if the water is consumed by humans therefore the nitrate contamination does pose risk to groundwater users in the surrounding area if consumed (SANS241-1:2015). The high vulnerability rating also adds to the risk, due to the fact that surface pollutants can move relatively quickly into the groundwater in a karst aquifer via sinkholes and other features in karst environments.

The karst aquifer in the Chuniespoort Group is known to be compartmentalised by intersecting dolomite dykes. This is quite clear form the dyke intersecting the quarry at PPC Mooiplaas and from Meyer (2014) these dykes present as barriers for groundwater. Therefore, it is possible that the NO_3^- would only impact the local compartment however this will need to be further investigated.

6. Conclusion

Characterisation of the surface water and groundwater found in and around PPC Mooiplaas was done by collecting inorganic chemistry data and isotopic data. It was found that the groundwater and the surface water at PPC Mooiplaas is mainly characterised by Ca^{2+}-Mg^{2+}-HCO_3^- type of water. The groundwater is mainly freshly recharged groundwater with lower average values of pH than the surface water. When the inorganic chemistry results of PPC Mooiplaas was compared to the surrounding karts aquifer chemistry it was seen that the mine has high amounts of NO_3^- in it. It was also seen that the Hennops River is contaminated by sewage due to the high concentrations of NH_4^+ and very small amounts of NO_3^-. This indicates that the NO_3^- contamination caused by PPC Mooiplaas has a very small impact on the river but it still has a substantial impact on the groundwater downgradient of the mine. The hydrogeochemical at PPC Mooiplaas is consistent with the understanding of what groundwater in a karst environment is. The study also showed that mining dolomite at PPC Mooiplaas does not have detrimental environmental effects besides elevated NO_3^-.

In addition to assessing the hydrogeochemistry of the water samples collected at PPC Mooiplaas stable isotopes were used to identify the source and possible pathways of the water in the study area. The isotope data indicated that the WPS water is freshly recharged groundwater with the Expl BHs possibly being the source of water seeping at the WPS. The isotope data also showed that the wall leaks, WPWS and EPWS both have a component of SsD since both these sampling locations deviate from the LMWL. The major surface water bodies e.g. the WP, EP and the FD is groundwater with a slight evaporation signature.

Recommendations

PPC Mooiplaas is a great example of the effects a dolomite mine has on a karst aquifer with the main impact being an increase in NO_3^- concentration. The following is recommended for further studies at the study area:

- High amounts of NO_3^- can cause serious negative effects to human health if consumed therefore, it is recommended that the PPC Mooiplaas treats the water for NO_3^-.
- PPC Mooiplaas would be ideal to conduct further studies at like such as tracer test along the dykes and faults which will be valuable to understand movement of contamination in a karst aquifer.

- It is possible that the NO_3^- contamination is isolated within the compartment since these compartments are known to be barriers. It is recommended that NO_3^- is used as a tracer to investigate if water and its contaminants move across these boundaries.
- A hydrocensus was not included in this study. It is recommended the a thorough hydrocensus is conducted with the main objective to obtain groundwater level data in the surrounding area. This will enable a better understanding of the groundwater flow direction in the study area.

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Appendix A: Pictures and co-ordinates of sampling locations

Table 9: Pictures and co-ordinates of sampling locations.

Sampling location	**Latitude (DD, WGS 84)**	**Longitude (DD, WGS, 84)**	**Picture**
Plant Inlet (PI)	-25.797697	28.079328	
Slurry Dam (SyD)	-25.797533	28.079606	
MDV Slurry Dam (SyD)	-25.794968	28.079742	

Sampling location	Latitude (DD, WGS 84)	Longitude (DD, WGS, 84)	Picture
Slimes Dam (SsD)	-25.801952	28.075477	
West Pit (WP)	-25.8063	28.07168	
East Pit (EP)	-25.806593	28.072849	

Sampling location	Latitude (DD, WGS 84)	Longitude (DD, WGS, 84)	Picture
Fish Dam (FD)	-25.808208	28.075152	
West Pit Seep (WPS)	-25.807491	28.067474	
Exploration Borehole North (Expl BH N)	-25.80596	28.065214	

Sampling location	Latitude (DD, WGS 84)	Longitude (DD, WGS, 84)	Picture
Exploration Borehole South (Expl BH S)	-25.807661	28.065314	
West Pit Wall Seep (WPWS)	-25.804688	28.072908	

Sampling location	**Latitude (DD, WGS 84)**	**Longitude (DD, WGS, 84)**	**Picture**
East Pit Wall Seep (EPWS)	-25.805163	28.074698	
Groundwater Flow 1 (GWF1)	-25.805163	28.074698	

Sampling location	Latitude (DD, WGS 84)	Longitude (DD, WGS, 84)	Picture
Groundwater Flow 12 (GWF12)	-25.80757	28.07333	
Groundwater Flow 2 (GWF2)	-25.817798	28.072965	No photo available
Groundwater Flow 13 (GWF13)	-25.80697	28.07266	No photo available
Hennops River Upstream (HRUS)	-25.82131	28.07969	No photo available
Hennops River Downstream (HRDS)	-25.815787	28.026028	No photo available
Sump	-25.80796	28.076174	No photo available

Sampling location	Latitude (DD, WGS 84)	Longitude (DD, WGS, 84)	Picture
Rain	-25.802818	28.224256	

Appendix B: Data validation tables

Table 10: *Evaluation of inorganic chemical results of blank samples to the inorganic results of rain samples.*

Parameter	Unit	Rain samples		Test results of blank samples tested during study period					
		Minimum	Maximum	April Blank	May Blank	June Blank	July Blank	August Blank	September Blank
Evaluation method		2	4	Green = Less than the min. rainfall value	1	Yellow: Value between min. and max. of rainfall value	3	Red: value above max. of rainfall value	5
pH	-	5.9	6.63	6.58	6.51	6.53	6.22	6.41	6.54
EC	mS/m	1.79	4.6	1.06	0.312	1.16	1.52	0.8	1.13
TDS	mg/l	10	22	<10	<10	<10	<10	<10	<10
Alkalinity	mg CaCO3/l	2.44	3.28	<1.99	<1.99	<1.99	<1.99	<1.99	<1.99
TH	mg CaCO3/l	4	10	3	0	2	0	0	0
Cl^-	mg/l	0.859	2.04	1.36	0.666	<0.557	<0.557	0.625	0.589
SO_4^{2-}	mg/l	1.75	6.84	2.46	<0.141	0.84	0.842	0.899	<0.141
NO_3^--N	mg/l	0.338	1.23	0.228	0.253	<0.194	0.411	<0.194	0.416
PO_4^{3-}-P	mg/l	0.013	0.124	0.01	<0.005	0.018	0.044	0.049	0.042
F^-	mg/l	0.265	0.265	<0.263	<0.263	<0.263	<0.263	<0.263	<0.263
Br^-	mg/l	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.04
NH_4^+-N	mg/l	0.165	1.24	0.044	0.036	0.067	0.091	0.039	0.014
Ca^{2+}	mg/l	0.801	3.4	0.872	<0.082	0.601	<0.082	<0.082	<0.082
Mg^{2+}	mg/l	0.34	0.628	0.301	<0.077	<0.077	<0.077	<0.077	<0.077
Na^+	mg/l	0.309	1.09	0.909	0.043	<0.041	0.222	0.117	0.103

K^+	mg/l	0.121	1.33	<0.015	<0.015	<0.015	0.147	0.037	0.085

Table 11: Duplicate evaluation table by means of RPD calculation.

Parameter	Unit	FD	FD D	RPD	WPWS	WPWS D	RPD	PI	PI D	RPD	WP	WP D	RPD	SyD	SyD D	RPD
	Sampled Date	22-May-2017		%	23-Jun-2017		%	18-Jul-2017		%	17-Aug-2017		%	18-Sep-2017		%
Evaluation method		Green: RPD less than 10 %		<10	Yellow: RPD between 10 % to 20 %		10-20	Red: RPD value more than 20 %		>20						
pH	-	8.47	8.49	0.24	8.58	8.54	0.47	8.55	8.51	0.47	8.58	8.59	0.12	8.19	7.92	3.35
EC	mS/m	49.7	49.9	0.40	67.7	68.5	1.17	49.7	53.9	8.11	43.8	43.4	0.92	71.5	70.8	0.98
TDS	mg/l	317	322	1.56	418	431	3.06	326	321	1.55	330	327	0.91	424	423	0.24
Alkalinity	mg CaCO3/l	208	207	0.48	221	226	2.24	220	219	0.46	224	224	0.00	198	185	6.79
TH	mg CaCO3/l	275	281	2.16	343	374	8.65	270	273	1.10	288	282	2.11	345	349	1.15
Cl^-	mg/l	21.8	21.9	0.46	38.8	38.7	0.26	24	24.2	0.83	24.9	23.5	5.79	34.6	34	1.75
SO_4^{2-}	mg/l	30.2	30.5	0.99	35.6	35.2	1.13	31	26.4	16.03	25.9	24.7	4.74	32.7	33.1	1.22
NO_3^--N	mg/l	9.02	9.66	6.85	20.3	20.3	0.00	9.01	8.96	0.56	8.36	8.78	4.90	26.8	28.1	4.74
PO_4^{3-}-P	mg/l	0.014	0.016	13.33	0.017	0.015	12.50	0.056	0.043	26.26	0.051	0.043	17.02	0.044	0.045	2.25
F^-	mg/l	0.263	0.276	4.82	0.263	0.263	0.00	0.263	0.282	6.97	0.263	0.263	0.00	0.321	0.263	19.86
Br^-	mg/l	0.47	0.27	54.05	0.31	0.44	34.67	0.36	0.31	14.93	0.01	0.32	187.88	0.01	0.48	191.84
NH_4^+-N	mg/l	0.023	0.154	148.02	0.076	0.072	5.41	0.022	0.053	82.67	0.056	0.052	7.41	0.304	0.017	178.82
Ca^{2+}	mg/l	45.6	46.6	2.17	37.3	47.8	24.68	44.6	45	0.89	51.6	50.9	1.37	33.3	33.4	0.30
Mg^{2+}	mg/l	39.2	40	2.02	60.6	61.9	2.12	38.5	39	1.29	38.6	37.7	2.36	63.5	64.5	1.56
Na^+	mg/l	12.3	12.5	1.61	19.1	18.4	3.73	12.6	12.9	2.35	14.1	13.8	2.15	18.4	18.6	1.08
K^+	mg/l	0.626	0.624	0.32	1.05	1.32	22.78	0.601	0.614	2.14	0.617	0.606	1.80	1.86	1.82	2.17

Table 12: Evaluation of duplicate results for isotope analysis.

	d D (‰)		RPD %	d^{18}O (‰)		RPD %
Evaluation method	Same as in **Table 11**					
Plant Inlet (PI)	-15.6	-16.0	-1.21	-2.68	-2.67	0.12
Slurry Dam (SyD)	-13.4	-13.4	0.01	-2.23	-2.05	4.26
West Pit (WP)	-20.0	-19.7	0.79	-3.50	-3.74	-3.30
Fish Dam (FD)	-15.8	-15.6	0.46	-2.52	-2.79	-4.93
Exploration Borehole North (Expl BH N)	-27.5	-27.2	0.52	-4.79	-4.73	0.58
West Pit Wall Seep (WPWS)	-14.2	-14.1	0.39	-2.24	-2.27	-0.63
Groundwater Flow 1 (GWF1)	-19.3	-19.0	0.89	-3.37	-3.29	1.22
Groundwater Flow 12 (GWF12)	-16.5	-16.4	0.09	-2.84	-2.84	-0.08
May rain	-72.0	-72.6	-0.42	-9.88	-9.92	-0.21

Table 13: Evaluation of charge balance calculations for the results of the inorganic chemistry samples.

	Plant Inlet (PI)	Slurry Dam (SyD)	MDV Slurry Dam (MDV SyD)	Slimes Dam (SsD)	West Pit Seep (WPS)	West Pit (WP)	East Pit (EP)	Exploration Borehole N (Expl BH N)	Exploration Borehole S (Expl BH S)	West Pit Wall Seep (WPWS)	East Pit Wall Seep (EPWS)	Fish Dam (FD)	Rain	
	Charge Balance (%)													
Evaluation method	Same as in **Table 11**													
2015/04/22	-	-	-	-	1.01	-	-	-	-	-	-	-		
2017/04/12	0.79	4.5	0.42	1.47	1.44	2.06	0.45	2.64	0.59	-	-	3.31	December	8.15
2017/05/22	1.35	0.44	0.56	4.56	2.14	1.49	0.12	4.93	1.12	1.67	-	0.04	January	7.76
2017/06/23	0.03	2.8	1.59	1.64	3.91	0.83	1.62	-	-	0.02	0.97	2.31	February	3.12
2017/07/18	3.65	1.6	2.36	2.86	-	1.83	1.18	-	-	1.98	2.83	1.92	2017/02/21	2.92
2017/08/17	0.000217	2.93	2.29	4.2	-	0.51	1.26	-	0.68	2.32	4.09	0.01	March	0.66
2017/09/18	3.46	1.45	4.59	1.78	-	2.78	2.74	-	3.07	-	-	3.57	April	8.91
Duplicate	2.04	3.19	-	-	-	0.27	-	-	-	3.44	-	0.78		

Table 14: Evaluation of charge balance for inorganic chemistry results obtained from Aquatico.

	West Pit (WP)	East Pit (EP)	Fish Dam (FD)	Groundwater Flow 1 (GWF1)	Groundwater Flow 2 (GWF02)	Groundwater Flow 12 (GWF12)	Groundwater Flow 13 (GWF13)	Hennops River (HRUS)	Hennops River Downstream (HRDS)	Sump
	Charge Balance (%)									
Evaluation method	Same as **Table 11**									
2011/11/04	5.19	3.76	5.07	-	-	5.06	5.01	1.16	1.51	4.88
2012/03/01	3.13	5.1	4.55	-	-	2.61	4.27	3.44	3.61	6.92
2012/09/21	0.58	2.48	5.4	-	-	5.16	4.26	3.28	2.67	3.06
2012/12/11	1.45	4.48	4.37	-	-	3.77	2.21	1.97	4.17	-
2013/01/31	-	-	-	4.02	3.05	-	3.17	-	-	-
2013/02/27	-	-	-	4.59	3.76	3.79	-	-	-	-
2013/03/26	0.68	0.06	1.99	2.44	1.09	1.6	1.59	3.94	2.63	3.26
2013/04/25	-	-	-	0.05	5.01	0.12	-	-	-	-
2013/05/13	-	-	-	5.16	4.05	3.27	-	-	-	-
2013/06/24	1.13	2.37	1.55	0.22	2.59	1.95	3.97	3.04	2.59	-
2013/07/25	-	-	-	2.56	0.64	0.88	-	-	-	-
2013/09/19	0.81	1.06	2.51	1.51	2.25	2.45	-	-	-	-
2013/09/19	-	-	-	-	1.21	2.22	0.1	1.62	0.66	-
2013/10/22	-	-	-	2.42	2.11	1.62	-	-	-	-
2013/11/13	-	-	-	5.3	1.73	2.28	-	-	-	-
2013/12/12	0.05	0.32	0.78	0.6	0.51	4.02	5.14	0.84	2.26	6.78
2014/02/06	-	-	-	0.83	0.81	1.05	-	-	-	-
2014/02/27	-	-	-	3.11	1.02	1.1	-	-	-	-
2014/03/25	2.01	3.32	1.67	2.07	3.24	3.92	4.22	2.43	4.4	-

	West Pit (WP)	East Pit (EP)	Fish Dam (FD)	Groundwater Flow 1 (GWF1)	Groundwater Flow 2 (GWF02)	Groundwater Flow 12 (GWF12)	Groundwater Flow 13 (GWF13)	Hennops River (HRUS)	Hennops River Downstream (HRDS)	Sump
	Charge Balance (%)									
Evaluation method	Same as **Table 11**									
2014/04/24	-	-	-	3.87	4.98	2.68	-	-	-	-
2014/05/29	-	-	-	1.62	3.76	3.93	-	-	-	-
2014/06/05	3.7	4.94	4.29	1.33	5.12	4.2	2.84	1.32	2.16	-
2014/07/07	-	-	-	2.78	4.69	5.22	-	-	-	-
2014/08/28	-	-	-	1.5	2.37	0.32	-	-	-	-
2014/09/23	0.02	1.48	0.28	2.61	4.53	2.4	4.35	0.31	0.58	-
2014/10/15	-	-	-	0.78	0.22	1.22	-	-	-	-
2014/11/06	-	-	-	4.05	4.7	4.56	-	-	-	-
2014/12/11	1.12	1.21	1.26	3.53	1.55	1.24	2.97	4.89	1.46	-
2015/01/22	-	-	-	2.7	4.63	4.59	-	-	-	-
2015/02/18	-	-	-	3.57	4.31	3.33	-	-	-	-
2015/03/30	3.8	3.13	2.42	4.74	4.53	2.81	3.12	3.12	2.22	2.5
2015/04/22	-	-	-	0.14	0	0.41	-	2.12	-	-
2015/05/26	-	-	-	2.71	0.48	0.87	-	-	-	-
2015/06/22	2.34	3.94	4.77	0.59	4.61	3.28	0.12	2	2.02	0.69
2015/07/03	-	-	-	4.45	4.71	1.45	-	-	-	-
2015/08/25	-	-	-	4.41	1.05	4.34	-	-	-	-
2015/09/16	1.32	1.7	1.19	2.08	1.96	2.1	1.2	2.19	2.69	2.5
2015/10/23	-	-	-	1.72	0.67	1.3	-	-	-	-
2015/11/16	-	-	-	5.6	5.25	3.73	-	-	-	-
2015/12/04	2.41	3.12	1.48	5.15	1.37	3.74	4.12	0.89	0.56	4.17

	West Pit (WP)	East Pit (EP)	Fish Dam (FD)	Groundwater Flow 1 (GWF1)	Groundwater Flow 2 (GWF02)	Groundwater Flow 12 (GWF12)	Groundwater Flow 13 (GWF13)	Hennops River (HRUS)	Hennops River Downstream (HRDS)	Sump
	Charge Balance (%)									
Evaluation method	Same as **Table 11**									
2016/01/27	-	-	-	5.29	4.97	5.17	-	-	-	-
2016/02/18	-	-	-	3.88	2.17	2.51	-	-	-	-
2016/03/18	-	4.04	2.96	4.47	1.97	1.87	3.3	3.48	3.23	1.88
2016/04/22	-	-	-	4.44	5.2	4.72	-	-	-	-
2016/05/20	-	-	-	2.47	4.58	2.69	-	-	-	-
2016/06/10	1.4	1.73	1.07	0.86	0.67	2.03	2.08	0.18	0.35	1.88
2016/07/26	-	-	-	1.79	3.02	3.28	-	-	-	-
2016/08/12	-	-	-	0.27	0.55	0.2	-	-	-	-
2016/09/28	3.46	0.29	0.06	4.12	4.23	4.3	2.74	3.9	1.73	2.49
2016/10/20	-	-	-	3.23	0.63	2.82	-	-	-	-
2016/11/25	-	-	-	3.89	2.72	1.25	-	-	-	-
2016/12/12	3.13	5.02	3.81	4.92	4.6	4.84	3.96	4.71	3.43	1.1
2017/01/26	-	-	-	4.51	2.3	2.9	-	-	-	-
2017/02/09	-	-	-	0.77	1.15	3.11	-	-	-	-
2017/03/02	4.9	4.75	4.75	4.14	4.19	2.54	3.44	2.5	2.94	1.42
2017/04/18	-	-	-	4.18	1.31	0.35	-	-	-	-
2017/05/22	-	-	-	0.98	1.89	1.85	-	-	-	-
2017/06/19	1.23	1.17	1.44	0.84	2.72	3.29	3.04	1.46	1.86	0.18
2017/07/17	-	-	-	1.95	2.79	2.15	-	-	-	-
2017/08/17	-	-	-	2.6	1.45	1.5	-	-	-	-
2017/09/14	4.58	5.36	4.53	2.38	4.26	3.9	2.82	1.04	0.56	1.21

	West Pit (WP)	East Pit (EP)	Fish Dam (FD)	Groundwater Flow 1 (GWF1)	Groundwater Flow 2 (GWF02)	Groundwater Flow 12 (GWF12)	Groundwater Flow 13 (GWF13)	Hennops River (HRUS)	Hennops River Downstream (HRDS)	Sump
	Charge Balance (%)									
Evaluation method	Same as **Table 11**									
2017/10/13	-	-	-	1.55	1.39	2.65	-	-	-	-

Appendix C: Physicochemical parameters

Table 15: Physicochemical parameters for the rainwater samples.

Parameter	Unit	Rain (n = 6)			
		Min	Max	Mean	SD
pH	-	5.90	6.63	6.18	0.28
EC	mS/m	1.79	4.60	3.20	1.32
TDS	mg/L	5.00	22.0	14.2	6.55
Alkalinity	mg $CaCO_3$/L	1.00	3.28	1.62	1.00
TH	mg $CaCO_3$/L	4.00	10.0	6.50	2.26
Cl^-	mg/L	0.86	2.04	1.52	0.55
SO_4^{2-}	mg/L	1.75	6.84	4.18	1.67
NO_3^--N	mg/L	0.34	1.23	0.79	0.40
PO_4^{3-}-P	mg/L	0.01	0.12	0.07	0.04
F^-	mg/L	0.13	0.27	0.15	0.05
Br^-	mg/L	0.01	0.01	0.01	0.00
NH_4^+-N	mg/L	0.17	1.24	0.74	0.44
Ca^{2+}	mg/L	0.80	3.40	1.89	1.06
Mg^{2+}	mg/L	0.04	0.63	0.41	0.22
Na^+	mg/L	0.31	1.09	0.71	0.30
K^+	mg/L	0.12	1.33	0.67	0.47

Table 16: Physicochemical parameters for the sump water samples.

Parameter	Unit	Sump (n = 16)			
		Min	Max	Mean	SD
pH	-	7.25	8.54	7.81	0.41
EC	mS/m	22.9	99.2	56.6	18.0
TDS	mg/L	129	589	318	111
Alkalinity	mg $CaCO_3$/L	106	520	248	96.5
TH	mg $CaCO_3$/L	107	352	240	77.0
Cl^-	mg/L	6.54	48.7	26.5	11.4
SO_4^{2-}	mg/L	0.07	74.5	21.1	22.1
NO_3^--N	mg/L	0.03	7.75	0.86	1.87
PO_4^{3-}-P	mg/L	0.01	16.1	2.06	4.03
F^-	mg/L	0.01	13.7	3.28	3.63
Br^-	mg/L	-	-	-	-

NH_4^+-N	mg/L	0.23	1.67	0.46	0.36
Ca^{2+}	mg/L	17.7	67.4	38.8	12.3
Mg^{2+}	mg/L	13.1	58.2	34.8	12.4
Na^+	mg/L	6.39	63.0	30.1	14.7
K^+	mg/L	1.78	28.5	10.1	7.86

Table 17: Physicochemical parameters for the water samples of the West Pit Wall Seep (WPWS) and East Pit Wall Seep (EPWS).

Parameter	Unit	West Pit Wall Seep (WPWS) (n = 5)				East Pit Wall Seep (EPWS) (n = 3)			
		Min	Max	Mean	SD	Min	Max	Mean	SD
pH	-	8.48	8.65	8.57	0.07	8.42	8.57	8.49	0.08
EC	mS/m	55.8	70.2	65.48	5.70	69.9	89.1	80.5	9.74
TDS	mg/L	418	449	434	11.1	534	563	553	16.2
Alkalinity	mg $CaCO_3$/L	221	233	229	5.34	220	237	226	9.54
TH	mg $CaCO_3$/L	343	374	360	13.6	437	452	442	8.39
Cl^-	mg/L	37.3	40.3	38.9	1.09	65.8	68.9	67.3	1.55
SO_4^{2-}	mg/L	34.2	40.8	36.7	2.64	75.0	80.2	76.7	3.00
NO_3^--N	mg/L	19.8	23.6	21.2	1.58	24.7	29.3	27.1	2.31
PO_4^{3-}-P	mg/L	0.01	0.05	0.03	0.02	0.02	0.05	0.04	0.02
F^-	mg/L	0.13	0.13	0.13	0.00	0.13	0.13	0.13	0.00
Br^-	mg/L	0.31	0.65	0.48	0.15	0.47	0.77	0.58	0.16
NH_4^+-N	mg/L	0.00	0.08	0.04	0.03	0.00	0.07	0.04	0.03
Ca^{2+}	mg/L	37.3	52.0	45.8	5.37	68.4	76.0	71.0	4.36
Mg^{2+}	mg/L	57.7	61.9	59.6	1.63	63.6	64.9	64.4	0.70
Na^+	mg/L	16.7	19.1	17.6	1.08	14.3	15.7	14.9	0.71
K^+	mg/L	1.05	1.32	1.18	0.11	0.02	0.33	0.20	0.16

Table 18: Physicochemical parameters for the water samples of the Slurry Dam (SyD), MDV Slurry Dam (MDV SyD) and Slimes Dam (SsD).

Parameter	Unit	Slurry Dam (SyD) (n = 7)				MDV Slurry Dam (MDV SyD) (n = 6)				Slimes Dam (SsD) (n = 6)			
		Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
pH	-	7.92	8.73	8.43	0.29	8.61	9.02	8.77	0.15	8.38	8.86	8.59	0.18
EC	mS/m	53.9	71.5	61.0	8.00	46.0	67.3	57.1	8.64	16.3	71.9	44.8	21.7
TDS	mg/L	356	436	401	30.4	299	431	359	47.2	102	449	289	147
Alkalinity	mg $CaCO_3$/L	183	229	205	17.6	197	254	225	22.1	69.1	229	163	71.2
TH	mg $CaCO_3$/L	290	349	318	23.0	262	349	308	34.8	89.0	349	235	115
Cl^-	mg/L	30.7	41.5	35.4	3.90	26.6	54.1	37.8	10.9	6.76	47.5	26.1	16.5
SO_4^{2-}	mg/L	30.6	37.2	32.7	2.16	28.2	35.5	32.0	2.88	14.8	41.0	29.2	9.77
NO_3^--N	mg/L	12.5	28.8	21.9	6.70	7.21	15.4	10.8	2.77	1.72	23.7	12.3	9.44
PO_4^{3-}-P	mg/L	0.01	0.06	0.04	0.02	0.01	0.12	0.05	0.04	0.01	0.05	0.03	0.02
F^-	mg/L	0.13	0.35	0.19	0.10	0.13	0.35	0.21	0.09	0.13	0.38	0.23	0.11
Br^-	mg/L	0.01	0.48	0.07	0.18	0.01	0.50	0.19	0.19	0.01	0.46	0.09	0.18
NH_4^+-N	mg/L	0.02	2.61	1.10	1.03	0.02	0.28	0.13	0.11	0.02	1.03	0.37	0.40
Ca^{2+}	mg/L	27.6	37.0	32.2	3.56	10.3	33.7	19.6	9.51	11.9	34.2	20.9	8.42
Mg^{2+}	mg/L	51.3	64.5	57.8	5.45	48.5	77.7	62.8	12.7	14.5	70.9	44.4	24.4
Na^+	mg/L	14.8	18.6	16.0	1.51	14.1	21.4	17.7	3.23	3.20	19.8	12.0	7.38
K^+	mg/L	1.81	3.89	2.50	0.85	1.45	7.28	3.16	2.15	1.19	3.47	2.04	0.81

Table 19: Physicochemical parameters for the water samples of the Plant Inlet (PI), West Pit (WP), East Pit (EP) and Fish Dam (FD).

Parameter	Unit	Plant Inlet (PI) (n = 7)				West Pit (WP) (n = 29)				East Pit (EP) (n = 29)				Fish Dam (FD) (n = 30)			
		Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
pH	-	8.38	8.76	8.52	0.13	8.20	8.79	8.47	0.14	8.28	8.72	8.52	0.09	8.11	8.72	8.39	0.15
EC	mS/m	43.7	56.0	50.5	4.54	43.4	60.0	52.3	3.88	44.0	62.5	53.4	3.90	44.1	61.0	53.0	3.85
TDS	mg/L	303	341	322	12.1	237	361	306	27.2	255	350	307	21.5	252	356	308	22.9
Alkalinity	mg $CaCO_3$/L	203	223	212	8.60	156	228	203	16.1	141	227	198	16.8	175	245	207	14.6
TH	mg $CaCO_3$/L	258	287	275	10.0	231	332	275	19.5	239	323	280	18.3	240	335	279	20.2
Cl^-	mg/L	20.7	27.6	23.6	2.15	15.6	26.7	21.4	2.65	16.6	27.7	22.7	2.74	16.0	28.8	22.8	2.60
SO_4^{2-}	mg/L	26.4	47.1	31.8	6.94	21.4	43.0	27.4	5.25	23.0	48.2	32.5	6.57	26.1	43.8	32.5	5.08
NO_3^--N	mg/L	7.63	9.55	8.64	0.65	7.06	14.9	9.75	1.43	7.08	16.3	9.74	2.12	0.37	12.4	7.48	2.33
PO_4^{3-}-P	mg/L	0.01	0.11	0.05	0.03	0.01	0.13	0.03	0.03	0.00	0.12	0.03	0.03	0.00	1.78	0.09	0.32
F^-	mg/L	0.13	0.31	0.18	0.08	0.09	1.53	0.21	0.26	0.09	0.93	0.20	0.15	0.09	0.70	0.21	0.11
Br^-	mg/L	0.21	0.43	0.33	0.08	0.01	0.36	0.20	0.15	0.01	0.50	0.23	0.18	0.04	0.47	0.25	0.15
NH_4^+-N	mg/L	0.02	0.24	0.09	0.08	0.01	0.34	0.11	0.09	0.01	0.23	0.06	0.05	0.01	0.80	0.10	0.15
Ca^{2+}	mg/L	41.7	47.6	45.2	1.93	35.5	53.5	48.2	4.34	31.1	51.1	44.6	4.49	33.8	51.1	44.2	4.40
Mg^{2+}	mg/L	37.5	40.9	39.4	1.24	33.1	50.2	37.5	3.24	35.1	52.8	40.9	4.24	35.2	51.8	40.9	3.59
Na^+	mg/L	12.6	14.1	13.1	0.56	6.00	14.8	12.2	2.29	5.62	15.4	12.2	1.99	6.30	15.3	12.4	2.01
K^+	mg/L	0.60	0.81	0.71	0.08	0.02	1.20	0.60	0.22	0.02	1.36	0.73	0.30	0.02	1.52	0.74	0.28

Table 20: Physicochemical parameters for the water samples of Groundwater Flow 1 (GWF1), Groundwater Flow 2 (GWF2), Groundwater Flow (12) and Groundwater Flow 13 (GWF13).

Parameter	Unit	Groundwater Flow 1 (GWF1) (n = 57)				Groundwater Flow 2 (GWF2) (n = 59)				Groundwater Flow 12 (GWF12) (n = 62)				Groundwater Flow 13 (GWF13) (n = 24)			
		Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
pH	-	7.42	8.65	7.94	0.40	7.78	8.75	8.18	0.29	7.46	8.65	7.91	0.37	7.40	8.62	7.90	0.32
EC	mS/m	68.3	140	89.9	9.61	45.9	68.1	56.2	4.23	48.5	83.8	65.7	5.47	61.8	81.5	67.2	4.56
TDS	mg/L	413	807	547	61.1	287	360	326	14.0	272	429	383	26.0	320	413	376	25.5
Alkalinity	mg $CaCO_3$/L	254	393	320	35.9	192	245	218	14.0	227	295	263	14.2	235	283	263	12.0
TH	mg $CaCO_3$/L	389	664	494	42.9	254	358	299	21.1	271	409	361	21.9	323	404	362	20.0
Cl^-	mg/L	39.9	201	66.2	19.6	15.6	29.2	22.0	2.73	9.95	28.8	23.7	3.02	17.5	29.8	22.7	2.90
SO_4^{2-}	mg/L	45.9	122	84.6	13.0	19.0	42.9	32.4	5.08	25.4	49.6	40.5	4.71	33.7	47.9	39.9	3.94
NO_3^--N	mg/L	2.38	9.89	5.65	1.47	4.73	12.5	8.53	1.39	1.44	12.8	8.67	1.77	1.91	12.1	8.49	1.77
PO_4^{3-}-P	mg/L	0.00	0.33	0.05	0.05	0.00	0.10	0.03	0.02	0.00	0.13	0.03	0.02	0.00	0.12	0.03	0.03
F^-	mg/L	0.09	0.59	0.24	0.07	0.09	0.36	0.20	0.07	0.09	0.70	0.21	0.08	0.09	0.59	0.23	0.11
Br^-	mg/L	0.01	0.86	0.60	0.32	0.30	0.53	0.40	0.09	0.32	0.60	0.50	0.10	-	-	-	-
NH_4^+-N	mg/L	0.01	0.47	0.09	0.11	0.01	0.97	0.08	0.14	0.01	0.56	0.10	0.12	0.01	0.87	0.15	0.19
Ca^{2+}	mg/L	75.4	139	91.6	9.17	43.7	69.1	55.4	5.31	49.1	85.9	70.4	4.94	61.6	77.7	69.9	4.08
Mg^{2+}	mg/L	48.3	76.8	64.3	5.64	31.5	45.1	39.0	2.60	36.0	51.4	45.0	2.74	39.8	51.1	45.5	2.64
Na^+	mg/L	10.1	55.7	19.3	6.06	0.18	16.2	10.6	3.31	0.66	13.5	9.85	2.75	3.82	11.9	9.93	2.38
K^+	mg/L	0.08	1.87	1.05	0.42	0.02	1.45	0.55	0.32	0.02	1.79	0.88	0.36	0.02	6.58	1.35	1.68

Table 21: Physicochemical parameters for the water samples of the West Pit Seep (WPS), Exploration Borehole North (Expl BH N) and Exploration Borehole South (Expl BH S).

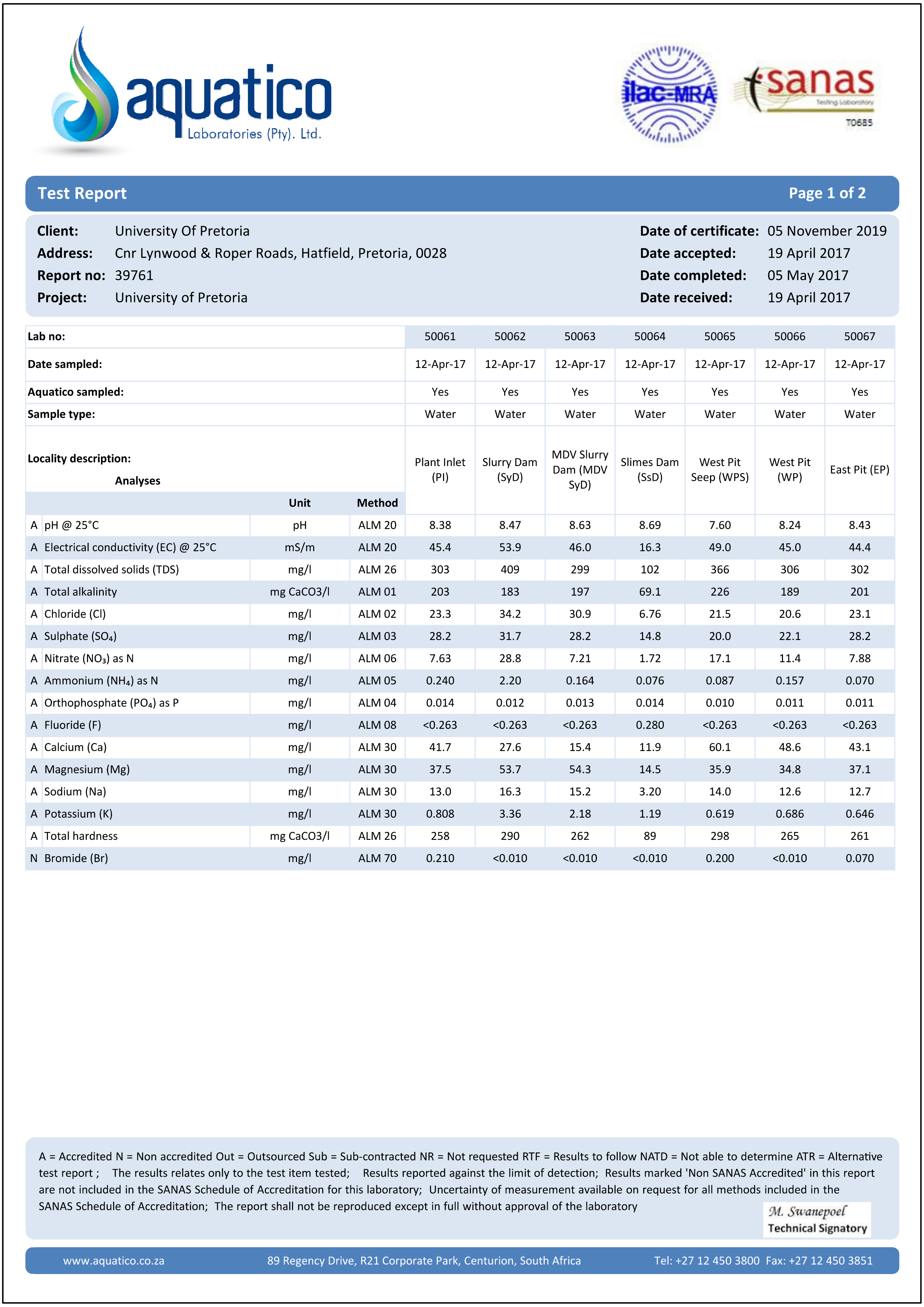
Parameter	Unit	West Pit Seep (WPS) (n = 4)				Exploration Borehole North (Expl BH N) (n = 2)				Exploration Borehole South (Expl BH S) (n = 4)			
		Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
pH	-	7.60	8.66	8.22	0.45	7.25	7.79	7.52	0.38	7.54	7.88	7.70	0.14
EC	mS/m	49.0	62.0	54.5	5.45	15.8	31.1	23.5	10.8	43.5	60.1	50.2	7.23
TDS	mg/L	316	366	341	21.3	102	206	154	73.5	272	328	307	26.4
Alkalinity	mg $CaCO_3$/L	187	226	211	18.6	101	205	153	73.5	255	291	277	16.2
TH	mg $CaCO_3$/L	278	298	288	8.66	100	151	126	36.1	261	325	296	30.4
Cl^-	mg/L	20.9	23.2	21.9	0.98	1.87	3.51	2.69	1.16	2.84	5.62	4.16	1.14
SO_4^{2-}	mg/L	20.0	27.8	24.1	3.36	0.07	3.95	2.01	2.74	16.2	35.2	26.4	10.07
NO_3^--N	mg/L	9.68	18.0	13.9	4.31	0.10	1.49	0.79	0.98	0.10	1.68	0.49	0.79
PO_4^{3-}-P	mg/L	0.01	0.03	0.02	0.01	0.02	1.10	0.56	0.76	0.01	0.05	0.03	0.02
F^-	mg/L	0.13	0.24	0.16	0.05	0.13	0.34	0.24	0.15	0.13	0.34	0.27	0.09
Br^-	mg/L	0.12	0.47	0.26	0.18	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.00
NH_4^+-N	mg/L	0.02	0.14	0.08	0.05	0.23	10.2	5.21	7.05	3.30	6.44	4.37	1.41
Ca^{2+}	mg/L	48.1	60.1	53.7	5.30	21.4	35.9	28.7	10.3	51.8	61.6	57.3	4.82
Mg^{2+}	mg/L	33.8	39.8	37.3	2.98	11.3	14.9	13.1	2.55	32.0	41.6	37.2	4.44
Na^+	mg/L	12.5	15.1	13.7	1.13	0.31	1.85	1.08	1.09	2.73	3.00	2.83	0.13
K^+	mg/L	0.37	0.84	0.55	0.22	1.22	5.05	3.14	2.71	2.28	3.13	2.67	0.37

Table 22:Physicochemical parameters for the water samples of the Hennops River Upstream (HRUS) and Hennops River Downstream (HRDS).

Parameter	Unit	Hennops River Upstream (HRUS) (n = 24)				Hennops River Downstream (HRDS) (n = 23)			
		Min	Max	Mean	SD	Min	Max	Mean	SD
pH		7.3	8.3	7.8	0.2	7.4	8.4	7.9	0.3
EC	-	32.8	120	69.1	20.5	32.8	103	66.1	15.8
TDS	mS/m	178	674	382	122	134	561	364	95.9
Alkalinity	mg/L	85.4	291	199	57.6	72.7	271	193	53.0
TH	mg/L	95.0	229	161	31.9	84.0	242	165	32.2
Cl^-	mg/L	19.1	205	66.2	49.8	17.4	170	57.9	34.1
SO_4^{2-}	mg/L	29.0	65.8	48.1	8.00	23.5	63.9	47.6	8.20
NO_3^--N	mg/L	0.20	2.70	1.50	0.80	0.20	3.90	2.10	1.00
PO_4^{3-}-P	mg/L	0.10	4.30	1.20	1.00	0.10	2.60	1.00	0.60
F^-	mg/L	0.10	0.30	0.20	0.10	0.20	0.30	0.30	0.00
Br^-	mg/L	-	-	-	-	-	-	-	-
NH_4^+-N	mg/L	1.20	28.1	10.2	7.30	0.70	24.0	9.10	7.00
Ca^{2+}	mg/L	25.7	58.5	38.7	7.40	20.9	60.4	39.2	7.30
Mg^{2+}	mg/L	7.40	21.6	15.7	3.60	7.70	22.2	16.3	3.60
Na^+	mg/L	22.8	166	64.7	33.8	13.2	126	58.7	23.0
K^+	mg/L	6.40	14.4	10.2	2.10	3.90	13.2	9.80	2.20

Appendix D: Chemistry laboratory results

April 2017: Report no. 39761



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Test Report **Page 1 of 2**

Client: University Of Pretoria
Address: Cnr Lynwood & Roper Roads, Hatfield, Pretoria, 0028
Report no: 39761
Project: University of Pretoria

Date of certificate: 05 November 2019
Date accepted: 19 April 2017
Date completed: 05 May 2017
Date received: 19 April 2017

	Lab no:			50061	50062	50063	50064	50065	50066	50067
	Date sampled:			12-Apr-17	12-Apr-17	12-Apr-17	12-Apr-17	12-Apr-17	12-Apr-17	12-Apr-17
	Aquatico sampled:			Yes	Yes	Yes	Yes	Yes	Yes	Yes
	Sample type:			Water	Water	Water	Water	Water	Water	Water
	Locality description: **Analyses**			Plant Inlet (PI)	Slurry Dam (SyD)	MDV Slurry Dam (MDV SyD)	Slimes Dam (SsD)	West Pit Seep (WPS)	West Pit (WP)	East Pit (EP)
		Unit	**Method**							
A	pH @ 25°C	pH	ALM 20	8.38	8.47	8.63	8.69	7.60	8.24	8.43
A	Electrical conductivity (EC) @ 25°C	mS/m	ALM 20	45.4	53.9	46.0	16.3	49.0	45.0	44.4
A	Total dissolved solids (TDS)	mg/l	ALM 26	303	409	299	102	366	306	302
A	Total alkalinity	mg CaCO3/l	ALM 01	203	183	197	69.1	226	189	201
A	Chloride (Cl)	mg/l	ALM 02	23.3	34.2	30.9	6.76	21.5	20.6	23.1
A	Sulphate (SO_4)	mg/l	ALM 03	28.2	31.7	28.2	14.8	20.0	22.1	28.2
A	Nitrate (NO_3) as N	mg/l	ALM 06	7.63	28.8	7.21	1.72	17.1	11.4	7.88
A	Ammonium (NH_4) as N	mg/l	ALM 05	0.240	2.20	0.164	0.076	0.087	0.157	0.070
A	Orthophosphate (PO_4) as P	mg/l	ALM 04	0.014	0.012	0.013	0.014	0.010	0.011	0.011
A	Fluoride (F)	mg/l	ALM 08	<0.263	<0.263	<0.263	0.280	<0.263	<0.263	<0.263
A	Calcium (Ca)	mg/l	ALM 30	41.7	27.6	15.4	11.9	60.1	48.6	43.1
A	Magnesium (Mg)	mg/l	ALM 30	37.5	53.7	54.3	14.5	35.9	34.8	37.1
A	Sodium (Na)	mg/l	ALM 30	13.0	16.3	15.2	3.20	14.0	12.6	12.7
A	Potassium (K)	mg/l	ALM 30	0.808	3.36	2.18	1.19	0.619	0.686	0.646
A	Total hardness	mg CaCO3/l	ALM 26	258	290	262	89	298	265	261
N	Bromide (Br)	mg/l	ALM 70	0.210	<0.010	<0.010	<0.010	0.200	<0.010	0.070

A = Accredited N = Non accredited Out = Outsourced Sub = Sub-contracted NR = Not requested RTF = Results to follow NATD = Not able to determine ATR = Alternative test report ; The results relates only to the test item tested; Results reported against the limit of detection; Results marked 'Non SANAS Accredited' in this report are not included in the SANAS Schedule of Accreditation for this laboratory; Uncertainty of measurement available on request for all methods included in the SANAS Schedule of Accreditation; The report shall not be reproduced except in full without approval of the laboratory

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Test Report

Client: University Of Pretoria
Address: Cnr Lynwood & Roper Roads, Hatfield, Pretoria, 0028
Report no: 39761
Project: University of Pretoria

Date of certificate: 05 November 2019
Date accepted: 19 April 2017
Date completed: 05 May 2017
Date received: 19 April 2017

Lab no:				50068	50069	50070	50071	50072
Date sampled:				18-Apr-17	18-Apr-17	12-Apr-17	12-Apr-17	12-Apr-17
Aquatico sampled:				Yes	Yes	Yes	Yes	Yes
Sample type:				Water	Water	Water	Water	Water
Locality description: **Analyses**				Exploration BH N (Expl BH N)	Exploration BH S (Expl BH S)	Stream Outside	Fish Dam (FD)	East Pit (EP) D
		Unit	**Method**					
A	pH @ 25°C	pH	ALM 20	7.79	7.54	8.31	8.38	8.55
A	Electrical conductivity (EC) @ 25°C	mS/m	ALM 20	15.8	43.5	43.6	44.4	48.6
A	Total dissolved solids (TDS)	mg/l	ALM 26	102	272	303	301	340
A	Total alkalinity	mg CaCO3/l	ALM 01	101	255	196	196	177
A	Chloride (Cl)	mg/l	ALM 02	1.87	5.62	21.9	23.6	31.6
A	Sulphate (SO_4)	mg/l	ALM 03	3.95	16.2	23.4	27.5	27.8
A	Nitrate (NO_3) as N	mg/l	ALM 06	<0.194	<0.194	8.90	7.44	16.7
A	Ammonium (NH_4) as N	mg/l	ALM 05	0.226	3.78	0.119	0.085	0.090
A	Orthophosphate (PO_4) as P	mg/l	ALM 04	0.022	0.010	0.011	0.010	0.010
A	Fluoride (F)	mg/l	ALM 08	<0.263	0.273	<0.263	<0.263	<0.263
A	Calcium (Ca)	mg/l	ALM 30	21.4	51.8	46.3	42.8	23.6
A	Magnesium (Mg)	mg/l	ALM 30	11.3	32.0	37.4	40.0	57.5
A	Sodium (Na)	mg/l	ALM 30	0.312	2.73	13.7	14.0	14.7
A	Potassium (K)	mg/l	ALM 30	1.22	2.77	1.22	0.807	2.42
A	Total hardness	mg CaCO3/l	ALM 26	100	261	269	271	296
N	Bromide (Br)	mg/l	ALM 70	0.020	<0.010	<0.010	0.250	0.200

A = Accredited N = Non accredited Out = Outsourced Sub = Sub-contracted NR = Not requested RTF = Results to follow NATD = Not able to determine ATR = Alternative test report ; The results relates only to the test item tested; Results reported against the limit of detection; Results marked 'Non SANAS Accredited' in this report are not included in the SANAS Schedule of Accreditation for this laboratory; Uncertainty of measurement available on request for all methods included in the SANAS Schedule of Accreditation; The report shall not be reproduced except in full without approval of the laboratory

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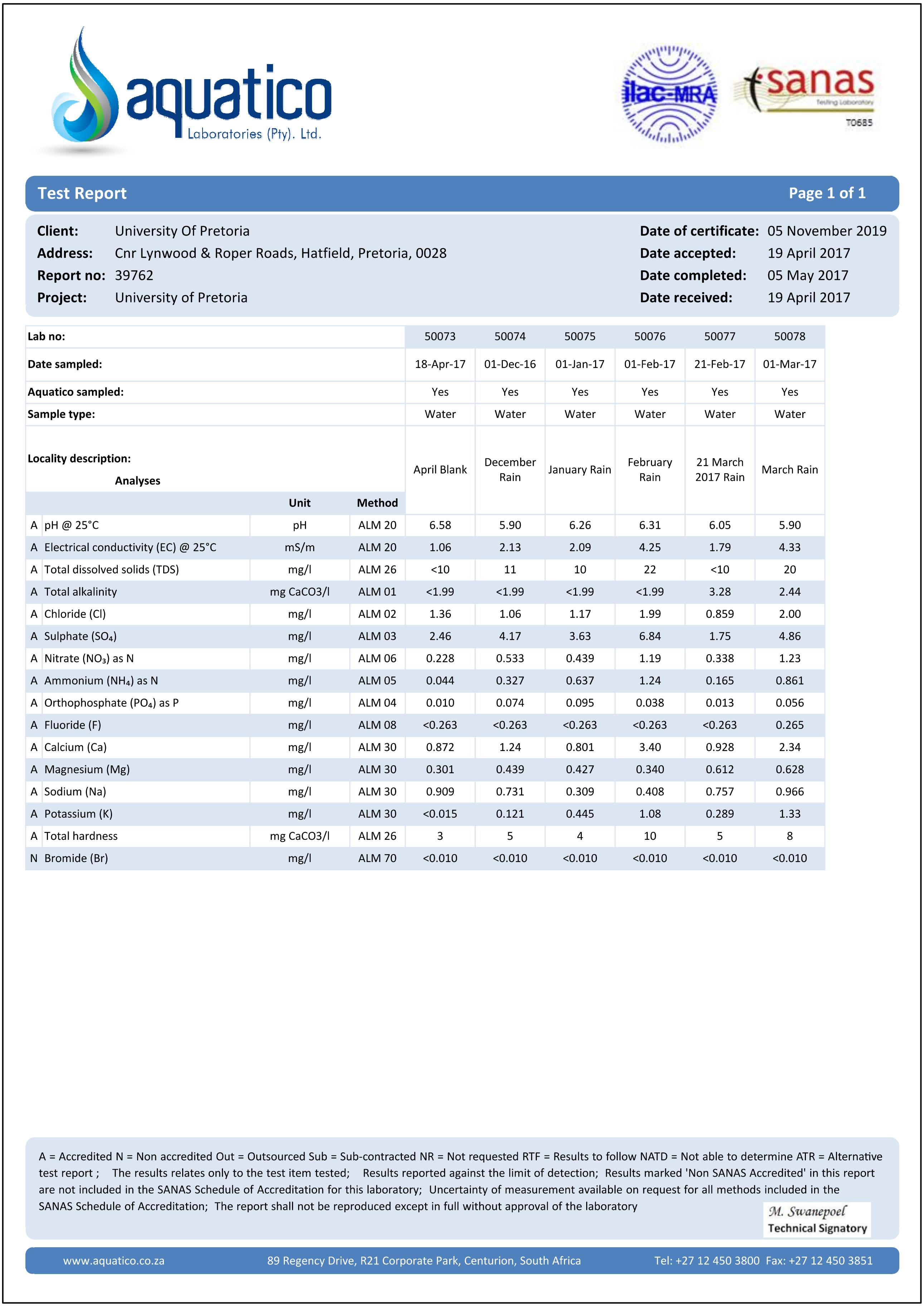

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Test Report **Page 1 of 1**

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Address: Cnr Lynwood & Roper Roads, Hatfield, Pretoria, 0028
Report no: 39762
Project: University of Pretoria

Date of certificate: 05 November 2019
Date accepted: 19 April 2017
Date completed: 05 May 2017
Date received: 19 April 2017

Lab no:				50073	50074	50075	50076	50077	50078
Date sampled:				18-Apr-17	01-Dec-16	01-Jan-17	01-Feb-17	21-Feb-17	01-Mar-17
Aquatico sampled:				Yes	Yes	Yes	Yes	Yes	Yes
Sample type:				Water	Water	Water	Water	Water	Water
Locality description:				April Blank	December Rain	January Rain	February Rain	21 March 2017 Rain	March Rain
	Analyses								
		Unit	**Method**						
A	pH @ 25°C	pH	ALM 20	6.58	5.90	6.26	6.31	6.05	5.90
A	Electrical conductivity (EC) @ 25°C	mS/m	ALM 20	1.06	2.13	2.09	4.25	1.79	4.33
A	Total dissolved solids (TDS)	mg/l	ALM 26	<10	11	10	22	<10	20
A	Total alkalinity	mg CaCO3/l	ALM 01	<1.99	<1.99	<1.99	<1.99	3.28	2.44
A	Chloride (Cl)	mg/l	ALM 02	1.36	1.06	1.17	1.99	0.859	2.00
A	Sulphate (SO_4)	mg/l	ALM 03	2.46	4.17	3.63	6.84	1.75	4.86
A	Nitrate (NO_3) as N	mg/l	ALM 06	0.228	0.533	0.439	1.19	0.338	1.23
A	Ammonium (NH_4) as N	mg/l	ALM 05	0.044	0.327	0.637	1.24	0.165	0.861
A	Orthophosphate (PO_4) as P	mg/l	ALM 04	0.010	0.074	0.095	0.038	0.013	0.056
A	Fluoride (F)	mg/l	ALM 08	<0.263	<0.263	<0.263	<0.263	<0.263	0.265
A	Calcium (Ca)	mg/l	ALM 30	0.872	1.24	0.801	3.40	0.928	2.34
A	Magnesium (Mg)	mg/l	ALM 30	0.301	0.439	0.427	0.340	0.612	0.628
A	Sodium (Na)	mg/l	ALM 30	0.909	0.731	0.309	0.408	0.757	0.966
A	Potassium (K)	mg/l	ALM 30	<0.015	0.121	0.445	1.08	0.289	1.33
A	Total hardness	mg CaCO3/l	ALM 26	3	5	4	10	5	8
N	Bromide (Br)	mg/l	ALM 70	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010

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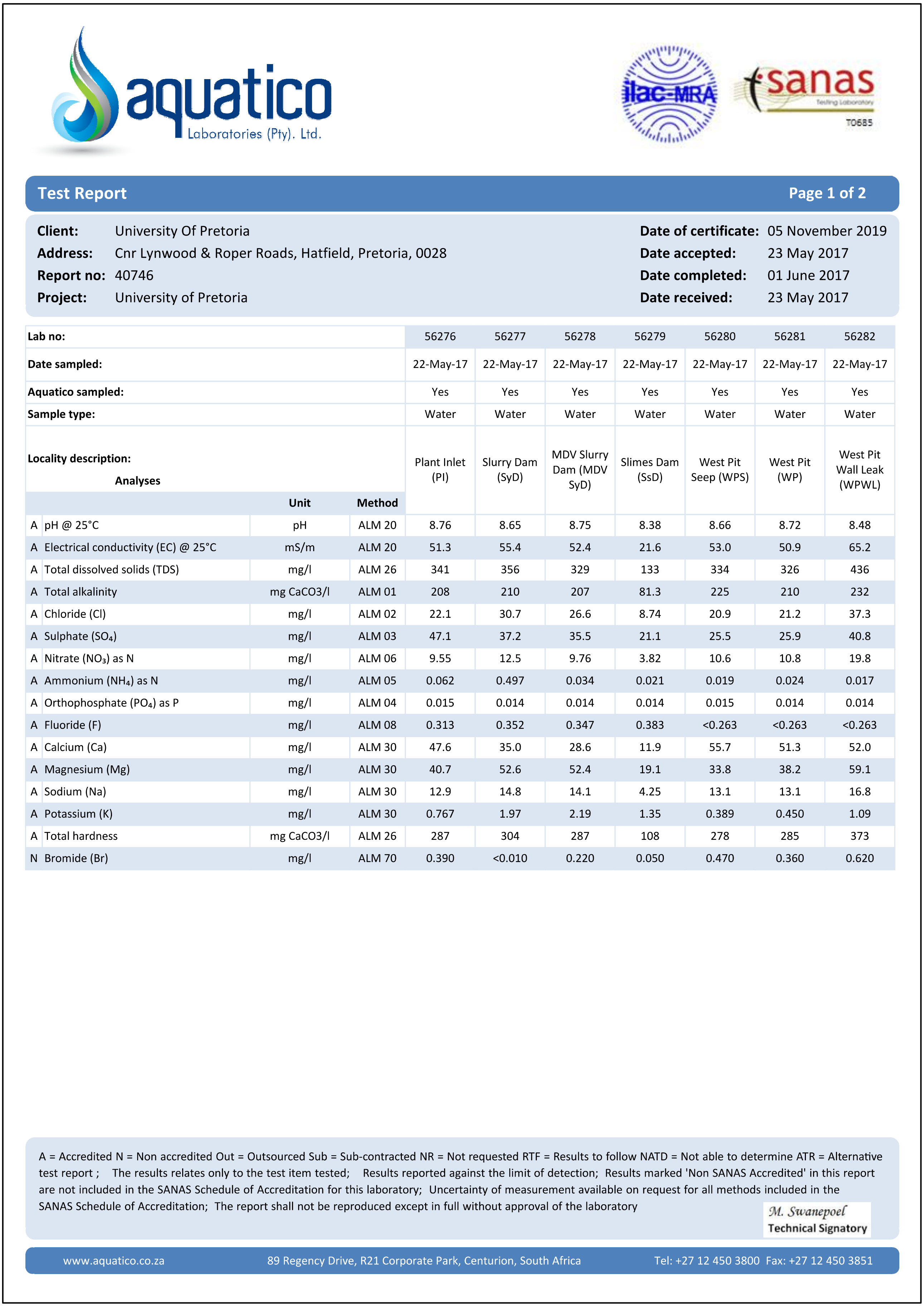
May 2017: Report no. 40746



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Test Report **Page 1 of 2**

Client: University Of Pretoria
Address: Cnr Lynwood & Roper Roads, Hatfield, Pretoria, 0028
Report no: 40746
Project: University of Pretoria

Date of certificate: 05 November 2019
Date accepted: 23 May 2017
Date completed: 01 June 2017
Date received: 23 May 2017

Lab no:				56276	56277	56278	56279	56280	56281	56282
Date sampled:				22-May-17	22-May-17	22-May-17	22-May-17	22-May-17	22-May-17	22-May-17
Aquatico sampled:				Yes	Yes	Yes	Yes	Yes	Yes	Yes
Sample type:				Water	Water	Water	Water	Water	Water	Water
Locality description:				Plant Inlet (PI)	Slurry Dam (SyD)	MDV Slurry Dam (MDV SyD)	Slimes Dam (SsD)	West Pit Seep (WPS)	West Pit (WP)	West Pit Wall Leak (WPWL)
	Analyses	**Unit**	**Method**							
A	pH @ 25°C	pH	ALM 20	8.76	8.65	8.75	8.38	8.66	8.72	8.48
A	Electrical conductivity (EC) @ 25°C	mS/m	ALM 20	51.3	55.4	52.4	21.6	53.0	50.9	65.2
A	Total dissolved solids (TDS)	mg/l	ALM 26	341	356	329	133	334	326	436
A	Total alkalinity	mg CaCO3/l	ALM 01	208	210	207	81.3	225	210	232
A	Chloride (Cl)	mg/l	ALM 02	22.1	30.7	26.6	8.74	20.9	21.2	37.3
A	Sulphate (SO_4)	mg/l	ALM 03	47.1	37.2	35.5	21.1	25.5	25.9	40.8
A	Nitrate (NO_3) as N	mg/l	ALM 06	9.55	12.5	9.76	3.82	10.6	10.8	19.8
A	Ammonium (NH_4) as N	mg/l	ALM 05	0.062	0.497	0.034	0.021	0.019	0.024	0.017
A	Orthophosphate (PO_4) as P	mg/l	ALM 04	0.015	0.014	0.014	0.014	0.015	0.014	0.014
A	Fluoride (F)	mg/l	ALM 08	0.313	0.352	0.347	0.383	<0.263	<0.263	<0.263
A	Calcium (Ca)	mg/l	ALM 30	47.6	35.0	28.6	11.9	55.7	51.3	52.0
A	Magnesium (Mg)	mg/l	ALM 30	40.7	52.6	52.4	19.1	33.8	38.2	59.1
A	Sodium (Na)	mg/l	ALM 30	12.9	14.8	14.1	4.25	13.1	13.1	16.8
A	Potassium (K)	mg/l	ALM 30	0.767	1.97	2.19	1.35	0.389	0.450	1.09
A	Total hardness	mg CaCO3/l	ALM 26	287	304	287	108	278	285	373
N	Bromide (Br)	mg/l	ALM 70	0.390	<0.010	0.220	0.050	0.470	0.360	0.620

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Client: University Of Pretoria
Address: Cnr Lynwood & Roper Roads, Hatfield, Pretoria, 0028
Report no: 40746
Project: University of Pretoria

Date of certificate: 05 November 2019
Date accepted: 23 May 2017
Date completed: 01 June 2017
Date received: 23 May 2017

	Lab no:			56283	56284	56285	56286	56287	56288
	Date sampled:			22-May-17	22-May-17	22-May-17	22-May-17	22-May-17	22-May-17
	Aquatico sampled:			Yes	Yes	Yes	Yes	Yes	Yes
	Sample type:			Water	Water	Water	Water	Water	Water
	Locality description:			East Pit (EP)	Fish Dam (FD)	Outside Stream	Exploration BH N (Expl BH N)	Exploration BH S (Expl BH S)	Fish Dam (FD) D
	Analyses	**Unit**	**Method**						
A	pH @ 25°C	pH	ALM 20	8.47	8.47	8.68	7.25	7.88	8.49
A	Electrical conductivity (EC) @ 25°C	mS/m	ALM 20	50.2	49.7	48.6	31.1	50.8	49.9
A	Total dissolved solids (TDS)	mg/l	ALM 26	325	317	315	206	302	322
A	Total alkalinity	mg CaCO3/l	ALM 01	209	208	203	205	274	207
A	Chloride (Cl)	mg/l	ALM 02	22.3	21.8	22.8	3.51	4.10	21.9
A	Sulphate (SO_4)	mg/l	ALM 03	31.1	30.2	31.2	<0.141	19.3	30.5
A	Nitrate (NO_3) as N	mg/l	ALM 06	9.94	9.02	9.10	1.49	1.68	9.66
A	Ammonium (NH_4) as N	mg/l	ALM 05	0.021	0.023	0.042	10.2	6.44	0.154
A	Orthophosphate (PO_4) as P	mg/l	ALM 04	0.016	0.014	0.014	1.10	0.020	0.016
A	Fluoride (F)	mg/l	ALM 08	<0.263	<0.263	<0.263	0.341	0.337	0.276
A	Calcium (Ca)	mg/l	ALM 30	47.2	45.6	43.9	35.9	54.6	46.6
A	Magnesium (Mg)	mg/l	ALM 30	39.8	39.2	40.0	14.9	35.0	40.0
A	Sodium (Na)	mg/l	ALM 30	12.5	12.3	12.5	1.85	2.74	12.5
A	Potassium (K)	mg/l	ALM 30	0.609	0.626	0.470	5.05	3.13	0.624
A	Total hardness	mg CaCO3/l	ALM 26	282	275	274	151	280	281
N	Bromide (Br)	mg/l	ALM 70	0.500	0.470	0.260	<0.010	<0.010	0.270

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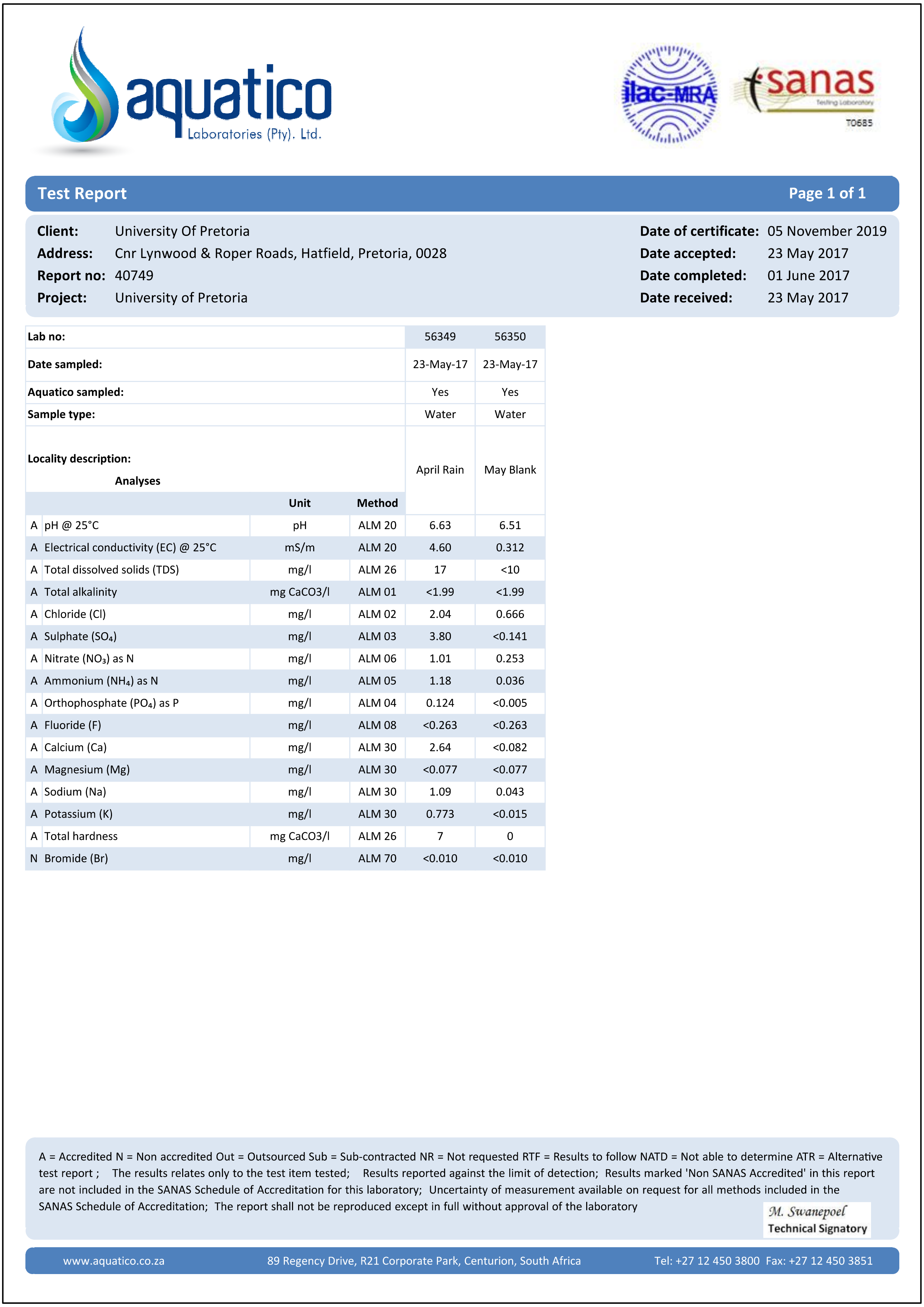
May 2017: Report no. 40749



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Test Report

Page 1 of 1

Client: University Of Pretoria
Address: Cnr Lynwood & Roper Roads, Hatfield, Pretoria, 0028
Report no: 40749
Project: University of Pretoria

Date of certificate: 05 November 2019
Date accepted: 23 May 2017
Date completed: 01 June 2017
Date received: 23 May 2017

Lab no:				56349	56350
Date sampled:				23-May-17	23-May-17
Aquatico sampled:				Yes	Yes
Sample type:				Water	Water
Locality description:				April Rain	May Blank
	Analyses	**Unit**	**Method**		
A	pH @ 25°C	pH	ALM 20	6.63	6.51
A	Electrical conductivity (EC) @ 25°C	mS/m	ALM 20	4.60	0.312
A	Total dissolved solids (TDS)	mg/l	ALM 26	17	<10
A	Total alkalinity	mg CaCO3/l	ALM 01	<1.99	<1.99
A	Chloride (Cl)	mg/l	ALM 02	2.04	0.666
A	Sulphate (SO_4)	mg/l	ALM 03	3.80	<0.141
A	Nitrate (NO_3) as N	mg/l	ALM 06	1.01	0.253
A	Ammonium (NH_4) as N	mg/l	ALM 05	1.18	0.036
A	Orthophosphate (PO_4) as P	mg/l	ALM 04	0.124	<0.005
A	Fluoride (F)	mg/l	ALM 08	<0.263	<0.263
A	Calcium (Ca)	mg/l	ALM 30	2.64	<0.082
A	Magnesium (Mg)	mg/l	ALM 30	<0.077	<0.077
A	Sodium (Na)	mg/l	ALM 30	1.09	0.043
A	Potassium (K)	mg/l	ALM 30	0.773	<0.015
A	Total hardness	mg CaCO3/l	ALM 26	7	0
N	Bromide (Br)	mg/l	ALM 70	<0.010	<0.010

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T0685

Test Report

Page 1 of 2

Client: University Of Pretoria
Address: Cnr Lynwood & Roper Roads, Hatfield, Pretoria, 0028
Report no: 41892
Project: University of Pretoria

Date of certificate: 05 November 2019
Date accepted: 26 June 2017
Date completed: 06 July 2017
Date received: 26 June 2017

Lab no:				62952	62953	62954	62955	62956	62957	62958
Date sampled:				23-Jun-17	23-Jun-17	23-Jun-17	23-Jun-17	23-Jun-17	23-Jun-17	23-Jun-17
Aquatico sampled:				Yes	Yes	Yes	Yes	Yes	Yes	Yes
Sample type:				Water	Water	Water	Water	Water	Water	Water
Locality description:				Plant Inlet (PI)	Slurry Dam (SyD)	MDV Slurry Dam (MDV SyD)	Slimes Dam (SsD)	West Pit Seep (WPS)	West Pit (WP)	West Pit Wall Leak (WPWL)
	Analyses	**Unit**	**Method**							
A	pH @ 25°C	pH	ALM 20	8.44	8.45	8.85	8.51	8.30	8.44	8.58
A	Electrical conductivity (EC) @ 25°C	mS/m	ALM 20	53.4	65.6	67.3	46.2	53.8	53.4	67.7
A	Total dissolved solids (TDS)	mg/l	ALM 26	314	393	390	263	316	312	418
A	Total alkalinity	mg CaCO3/l	ALM 01	204	210	247	166	205	206	221
A	Chloride (Cl)	mg/l	ALM 02	23.0	40.1	48.3	21.7	22.0	22.2	38.8
A	Sulphate (SO_4)	mg/l	ALM 03	31.3	31.4	31.8	30.3	22.9	23.5	35.6
A	Nitrate (NO_3) as N	mg/l	ALM 06	8.51	19.6	10.8	7.53	9.68	9.64	20.3
A	Ammonium (NH_4) as N	mg/l	ALM 05	0.147	1.63	0.232	0.577	0.082	0.078	0.076
A	Orthophosphate (PO_4) as P	mg/l	ALM 04	0.021	0.019	0.022	0.020	0.024	0.018	0.017
A	Fluoride (F)	mg/l	ALM 08	<0.263	<0.263	<0.263	<0.263	<0.263	<0.263	<0.263
A	Calcium (Ca)	mg/l	ALM 30	44.5	27.7	18.1	22.8	48.1	43.9	37.3
A	Magnesium (Mg)	mg/l	ALM 30	38.8	57.4	68.2	40.0	39.8	38.6	60.6
A	Sodium (Na)	mg/l	ALM 30	12.7	16.5	20.6	9.83	15.1	14.8	19.1
A	Potassium (K)	mg/l	ALM 30	0.684	2.79	3.68	2.09	0.365	0.262	1.05
A	Total hardness	mg CaCO3/l	ALM 26	271	306	326	222	284	269	343
N	Bromide (Br)	mg/l	ALM 70	0.330	<0.010	0.090	<0.010	0.120	0.120	0.310

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Test Report

Client: University Of Pretoria
Address: Cnr Lynwood & Roper Roads, Hatfield, Pretoria, 0028
Report no: 41892
Project: University of Pretoria

Date of certificate: 05 November 2019
Date accepted: 26 June 2017
Date completed: 06 July 2017
Date received: 26 June 2017

Lab no:				62959	62960	62961	62962	62963
Date sampled:				23-Jun-17	23-Jun-17	23-Jun-17	23-Jun-17	23-Jun-17
Aquatico sampled:				Yes	Yes	Yes	Yes	Yes
Sample type:				Water	Water	Water	Water	Water
Locality description:				East Pit Wall Leak (EPWL)	East Pit (EP)	Fish Dam (FD)	June Blank	West Pit Wall Leak (WPWL) D
	Analyses							
		Unit	**Method**					
A	pH @ 25°C	pH	ALM 20	8.42	8.42	8.34	6.53	8.54
A	Electrical conductivity (EC) @ 25°C	mS/m	ALM 20	82.4	53.5	53.6	1.16	68.5
A	Total dissolved solids (TDS)	mg/l	ALM 26	534	308	313	<10	431
A	Total alkalinity	mg CaCO3/l	ALM 01	221	205	204	<1.99	226
A	Chloride (Cl)	mg/l	ALM 02	65.8	23.3	23.1	<0.557	38.7
A	Sulphate (SO_4)	mg/l	ALM 03	75.0	27.8	27.7	0.840	35.2
A	Nitrate (NO_3) as N	mg/l	ALM 06	24.7	8.68	8.54	<0.194	20.3
A	Ammonium (NH_4) as N	mg/l	ALM 05	0.071	0.076	0.107	0.067	0.072
A	Orthophosphate (PO_4) as P	mg/l	ALM 04	0.016	0.016	0.016	0.018	0.015
A	Fluoride (F)	mg/l	ALM 08	<0.263	<0.263	<0.263	<0.263	<0.263
A	Calcium (Ca)	mg/l	ALM 30	68.4	43.5	44.8	0.601	47.8
A	Magnesium (Mg)	mg/l	ALM 30	64.9	37.2	40.4	<0.077	61.9
A	Sodium (Na)	mg/l	ALM 30	15.7	12.2	13.9	<0.041	18.4
A	Potassium (K)	mg/l	ALM 30	0.019	0.656	0.679	<0.015	1.32
A	Total hardness	mg CaCO3/l	ALM 26	438	262	278	2	374
N	Bromide (Br)	mg/l	ALM 70	0.470	0.210	0.270	<0.010	0.440

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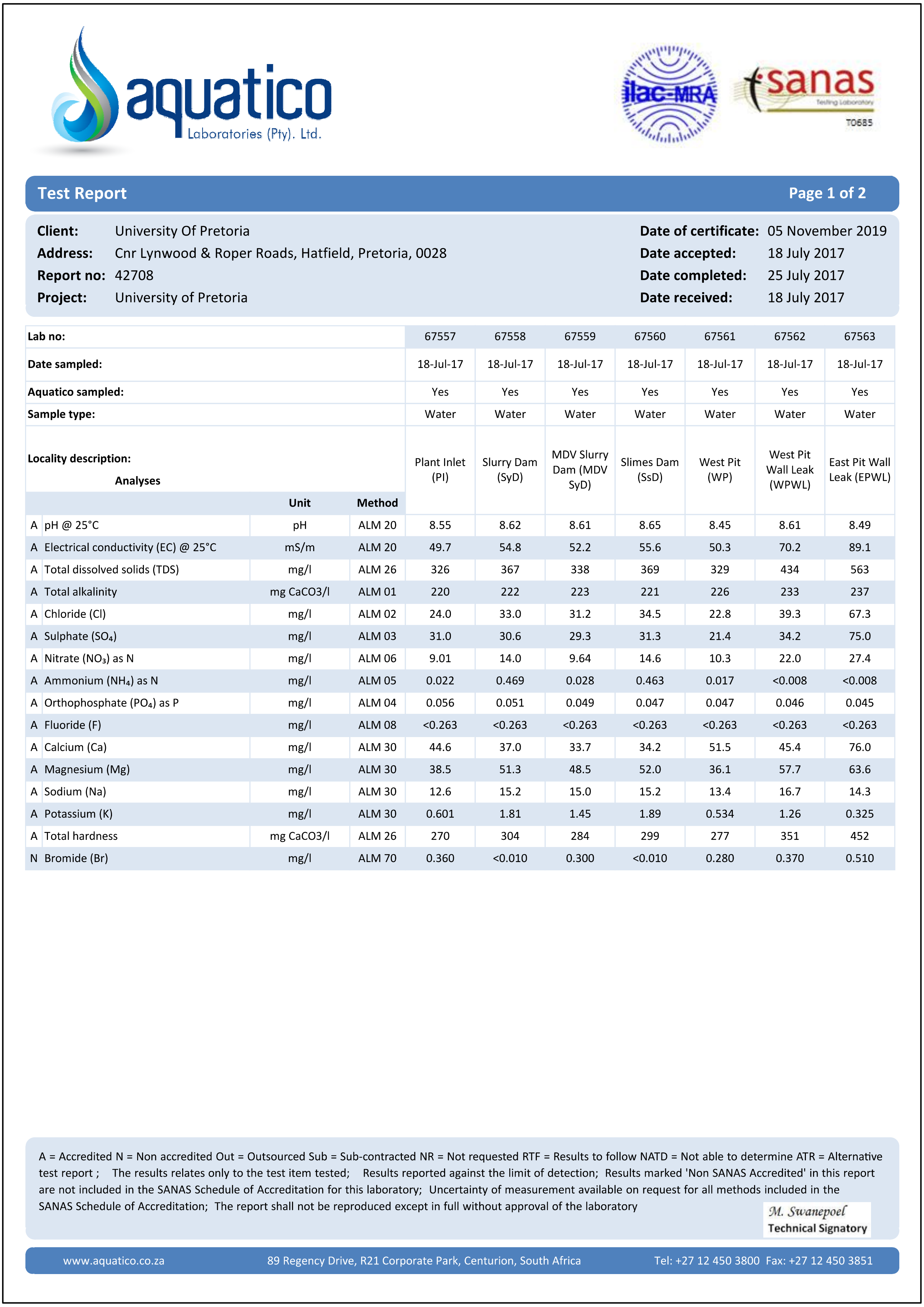
July 2017: Report no. 42708



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Test Report **Page 1 of 2**

Client: University Of Pretoria
Address: Cnr Lynwood & Roper Roads, Hatfield, Pretoria, 0028
Report no: 42708
Project: University of Pretoria

Date of certificate: 05 November 2019
Date accepted: 18 July 2017
Date completed: 25 July 2017
Date received: 18 July 2017

Lab no:				67557	67558	67559	67560	67561	67562	67563
Date sampled:				18-Jul-17	18-Jul-17	18-Jul-17	18-Jul-17	18-Jul-17	18-Jul-17	18-Jul-17
Aquatico sampled:				Yes	Yes	Yes	Yes	Yes	Yes	Yes
Sample type:				Water	Water	Water	Water	Water	Water	Water
Locality description:	**Analyses**			Plant Inlet (PI)	Slurry Dam (SyD)	MDV Slurry Dam (MDV SyD)	Slimes Dam (SsD)	West Pit (WP)	West Pit Wall Leak (WPWL)	East Pit Wall Leak (EPWL)
		Unit	**Method**							
A	pH @ 25°C	pH	ALM 20	8.55	8.62	8.61	8.65	8.45	8.61	8.49
A	Electrical conductivity (EC) @ 25°C	mS/m	ALM 20	49.7	54.8	52.2	55.6	50.3	70.2	89.1
A	Total dissolved solids (TDS)	mg/l	ALM 26	326	367	338	369	329	434	563
A	Total alkalinity	mg CaCO3/l	ALM 01	220	222	223	221	226	233	237
A	Chloride (Cl)	mg/l	ALM 02	24.0	33.0	31.2	34.5	22.8	39.3	67.3
A	Sulphate (SO_4)	mg/l	ALM 03	31.0	30.6	29.3	31.3	21.4	34.2	75.0
A	Nitrate (NO_3) as N	mg/l	ALM 06	9.01	14.0	9.64	14.6	10.3	22.0	27.4
A	Ammonium (NH_4) as N	mg/l	ALM 05	0.022	0.469	0.028	0.463	0.017	<0.008	<0.008
A	Orthophosphate (PO_4) as P	mg/l	ALM 04	0.056	0.051	0.049	0.047	0.047	0.046	0.045
A	Fluoride (F)	mg/l	ALM 08	<0.263	<0.263	<0.263	<0.263	<0.263	<0.263	<0.263
A	Calcium (Ca)	mg/l	ALM 30	44.6	37.0	33.7	34.2	51.5	45.4	76.0
A	Magnesium (Mg)	mg/l	ALM 30	38.5	51.3	48.5	52.0	36.1	57.7	63.6
A	Sodium (Na)	mg/l	ALM 30	12.6	15.2	15.0	15.2	13.4	16.7	14.3
A	Potassium (K)	mg/l	ALM 30	0.601	1.81	1.45	1.89	0.534	1.26	0.325
A	Total hardness	mg CaCO3/l	ALM 26	270	304	284	299	277	351	452
N	Bromide (Br)	mg/l	ALM 70	0.360	<0.010	0.300	<0.010	0.280	0.370	0.510

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Test Report

Page 2 of 2

Client: University Of Pretoria
Address: Cnr Lynwood & Roper Roads, Hatfield, Pretoria, 0028
Report no: 42708
Project: University of Pretoria

Date of certificate: 05 November 2019
Date accepted: 18 July 2017
Date completed: 25 July 2017
Date received: 18 July 2017

Lab no:				67564	67565	67566	67567
Date sampled:				18-Jul-17	18-Jul-17	18-Jul-17	18-Jul-17
Aquatico sampled:				Yes	Yes	Yes	Yes
Sample type:				Water	Water	Water	Water
Locality description:				East Pit (EP)	Fish Dam (FD)	July Blank	Plant Inlet (PI) D
	Analyses	**Unit**	**Method**				
A	pH @ 25°C	pH	ALM 20	8.53	8.53	6.22	8.51
A	Electrical conductivity (EC) @ 25°C	mS/m	ALM 20	54.1	54.0	1.52	53.9
A	Total dissolved solids (TDS)	mg/l	ALM 26	324	322	<10	321
A	Total alkalinity	mg CaCO3/l	ALM 01	219	220	<1.99	219
A	Chloride (Cl)	mg/l	ALM 02	24.4	24.1	<0.557	24.2
A	Sulphate (SO_4)	mg/l	ALM 03	26.3	26.1	0.842	26.4
A	Nitrate (NO_3) as N	mg/l	ALM 06	9.06	8.98	0.411	8.96
A	Ammonium (NH_4) as N	mg/l	ALM 05	0.058	0.151	0.091	0.053
A	Orthophosphate (PO_4) as P	mg/l	ALM 04	0.043	0.043	0.044	0.043
A	Fluoride (F)	mg/l	ALM 08	<0.263	<0.263	<0.263	0.282
A	Calcium (Ca)	mg/l	ALM 30	46.0	44.9	<0.082	45.0
A	Magnesium (Mg)	mg/l	ALM 30	39.5	39.1	<0.077	39.0
A	Sodium (Na)	mg/l	ALM 30	13.1	13.0	0.222	12.9
A	Potassium (K)	mg/l	ALM 30	0.632	0.649	0.147	0.614
A	Total hardness	mg CaCO3/l	ALM 26	278	273	0	273
N	Bromide (Br)	mg/l	ALM 70	0.300	0.090	<0.010	0.310

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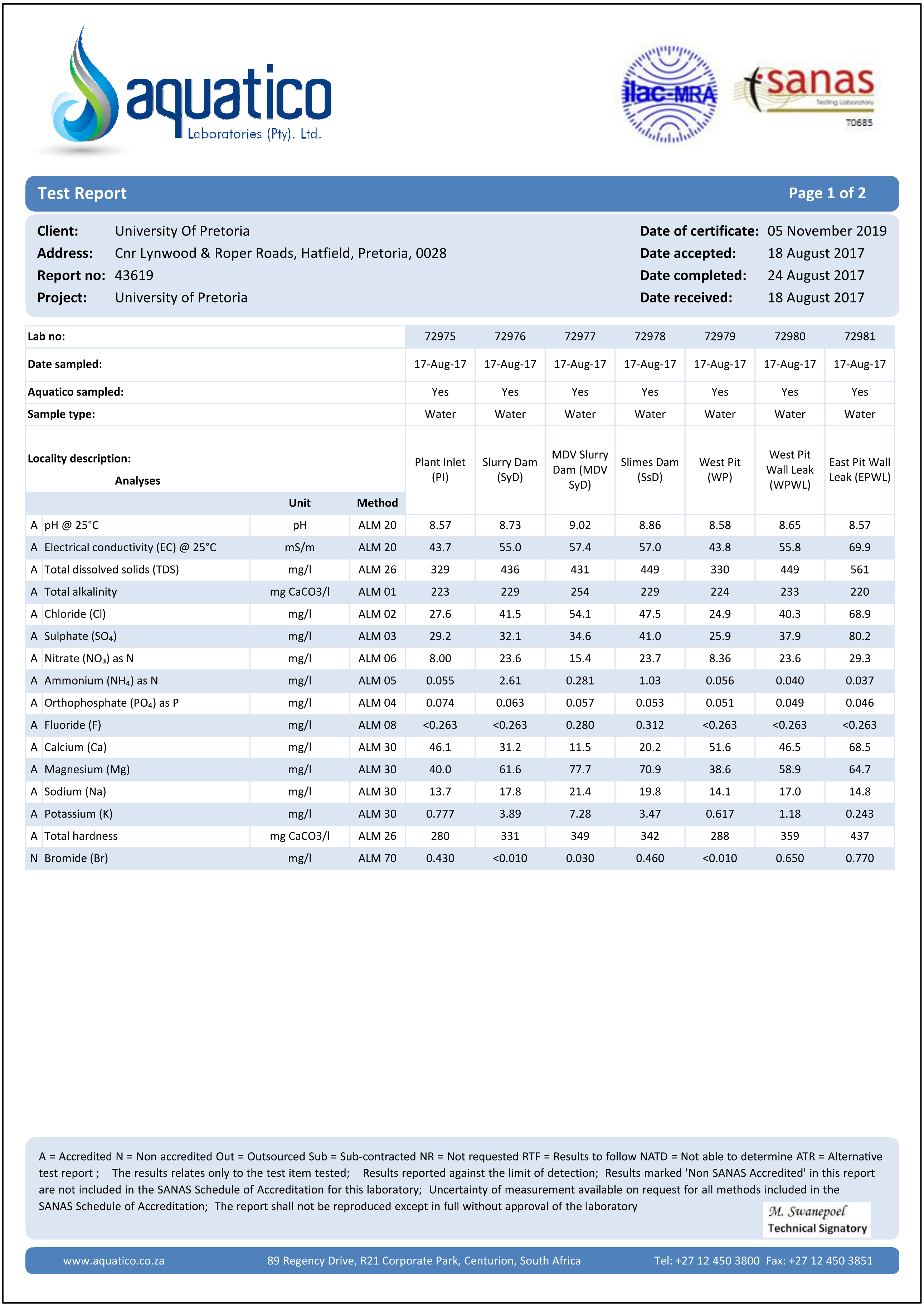
August 2017: Report no. 43619



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Test Report **Page 1 of 2**

Client: University Of Pretoria
Address: Cnr Lynwood & Roper Roads, Hatfield, Pretoria, 0028
Report no: 43619
Project: University of Pretoria

Date of certificate: 05 November 2019
Date accepted: 18 August 2017
Date completed: 24 August 2017
Date received: 18 August 2017

Lab no:				72975	72976	72977	72978	72979	72980	72981
Date sampled:				17-Aug-17	17-Aug-17	17-Aug-17	17-Aug-17	17-Aug-17	17-Aug-17	17-Aug-17
Aquatico sampled:				Yes	Yes	Yes	Yes	Yes	Yes	Yes
Sample type:				Water	Water	Water	Water	Water	Water	Water
Locality description:				Plant Inlet (PI)	Slurry Dam (SyD)	MDV Slurry Dam (MDV SyD)	Slimes Dam (SsD)	West Pit (WP)	West Pit Wall Leak (WPWL)	East Pit Wall Leak (EPWL)
	Analyses	**Unit**	**Method**							
A	pH @ 25°C	pH	ALM 20	8.57	8.73	9.02	8.86	8.58	8.65	8.57
A	Electrical conductivity (EC) @ 25°C	mS/m	ALM 20	43.7	55.0	57.4	57.0	43.8	55.8	69.9
A	Total dissolved solids (TDS)	mg/l	ALM 26	329	436	431	449	330	449	561
A	Total alkalinity	mg CaCO3/l	ALM 01	223	229	254	229	224	233	220
A	Chloride (Cl)	mg/l	ALM 02	27.6	41.5	54.1	47.5	24.9	40.3	68.9
A	Sulphate (SO_4)	mg/l	ALM 03	29.2	32.1	34.6	41.0	25.9	37.9	80.2
A	Nitrate (NO_3) as N	mg/l	ALM 06	8.00	23.6	15.4	23.7	8.36	23.6	29.3
A	Ammonium (NH_4) as N	mg/l	ALM 05	0.055	2.61	0.281	1.03	0.056	0.040	0.037
A	Orthophosphate (PO_4) as P	mg/l	ALM 04	0.074	0.063	0.057	0.053	0.051	0.049	0.046
A	Fluoride (F)	mg/l	ALM 08	<0.263	<0.263	0.280	0.312	<0.263	<0.263	<0.263
A	Calcium (Ca)	mg/l	ALM 30	46.1	31.2	11.5	20.2	51.6	46.5	68.5
A	Magnesium (Mg)	mg/l	ALM 30	40.0	61.6	77.7	70.9	38.6	58.9	64.7
A	Sodium (Na)	mg/l	ALM 30	13.7	17.8	21.4	19.8	14.1	17.0	14.8
A	Potassium (K)	mg/l	ALM 30	0.777	3.89	7.28	3.47	0.617	1.18	0.243
A	Total hardness	mg CaCO3/l	ALM 26	280	331	349	342	288	359	437
N	Bromide (Br)	mg/l	ALM 70	0.430	<0.010	0.030	0.460	<0.010	0.650	0.770

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Client: University Of Pretoria
Address: Cnr Lynwood & Roper Roads, Hatfield, Pretoria, 0028
Report no: 43619
Project: University of Pretoria

Date of certificate: 05 November 2019
Date accepted: 18 August 2017
Date completed: 24 August 2017
Date received: 18 August 2017

Lab no:				72982	72983	72984	72985	72986
Date sampled:				17-Aug-17	17-Aug-17	17-Aug-17	17-Aug-17	17-Aug-17
Aquatico sampled:				Yes	Yes	Yes	Yes	Yes
Sample type:				Water	Water	Water	Water	Water
Locality description:				East Pit (EP)	Fish Dam (FD)	August Blank	West Pit (WP) D	Exploration BH S (Expl BH S)
	Analyses	**Unit**	**Method**					
A	pH @ 25°C	pH	ALM 20	8.59	8.46	6.41	8.59	7.67
A	Electrical conductivity (EC) @ 25°C	mS/m	ALM 20	44.0	44.1	0.800	43.4	46.5
A	Total dissolved solids (TDS)	mg/l	ALM 26	330	324	<10	327	328
A	Total alkalinity	mg CaCO3/l	ALM 01	227	219	<1.99	224	291
A	Chloride (Cl)	mg/l	ALM 02	24.7	24.9	0.625	23.5	4.08
A	Sulphate (SO_4)	mg/l	ALM 03	29.1	28.4	0.899	24.7	35.2
A	Nitrate (NO_3) as N	mg/l	ALM 06	8.12	7.97	<0.194	8.78	<0.194
A	Ammonium (NH_4) as N	mg/l	ALM 05	0.036	0.049	0.039	0.052	3.30
A	Orthophosphate (PO_4) as P	mg/l	ALM 04	0.045	0.053	0.049	0.043	0.045
A	Fluoride (F)	mg/l	ALM 08	<0.263	<0.263	<0.263	<0.263	<0.263
A	Calcium (Ca)	mg/l	ALM 30	47.5	46.8	<0.082	50.9	61.0
A	Magnesium (Mg)	mg/l	ALM 30	40.2	40.1	<0.077	37.7	40.0
A	Sodium (Na)	mg/l	ALM 30	13.4	13.5	0.117	13.8	3.00
A	Potassium (K)	mg/l	ALM 30	0.636	0.946	0.037	0.606	2.49
A	Total hardness	mg CaCO3/l	ALM 26	284	282	0	282	317
N	Bromide (Br)	mg/l	ALM 70	<0.010	0.040	<0.010	0.320	<0.010

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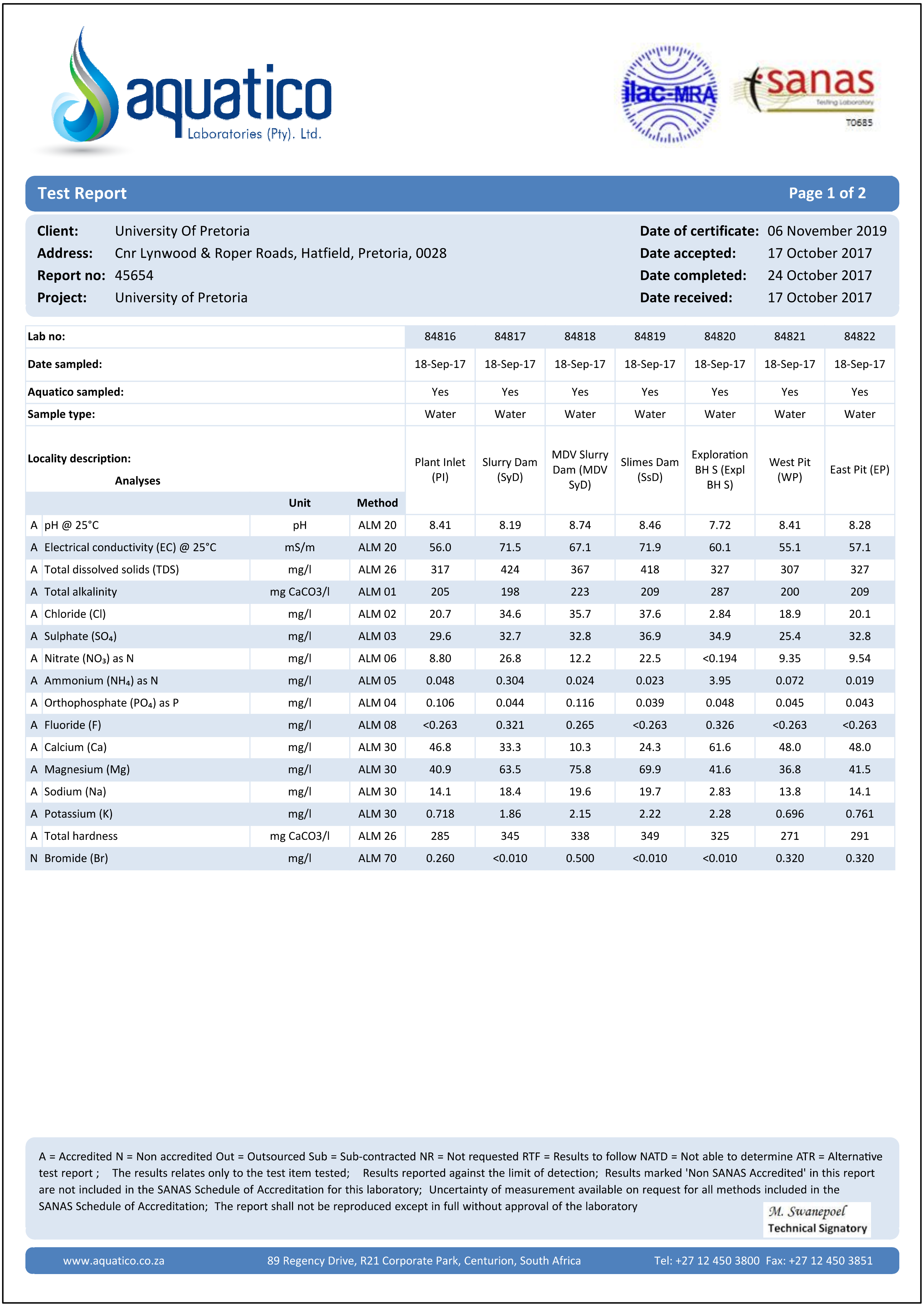
September 2017: Report no. 45654



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Test Report Page 1 of 2

Client: University Of Pretoria
Address: Cnr Lynwood & Roper Roads, Hatfield, Pretoria, 0028
Report no: 45654
Project: University of Pretoria

Date of certificate: 06 November 2019
Date accepted: 17 October 2017
Date completed: 24 October 2017
Date received: 17 October 2017

Lab no:				84816	84817	84818	84819	84820	84821	84822
Date sampled:				18-Sep-17	18-Sep-17	18-Sep-17	18-Sep-17	18-Sep-17	18-Sep-17	18-Sep-17
Aquatico sampled:				Yes	Yes	Yes	Yes	Yes	Yes	Yes
Sample type:				Water	Water	Water	Water	Water	Water	Water
Locality description:				Plant Inlet (PI)	Slurry Dam (SyD)	MDV Slurry Dam (MDV SyD)	Slimes Dam (SsD)	Exploration BH S (Expl BH S)	West Pit (WP)	East Pit (EP)
	Analyses	**Unit**	**Method**							
A	pH @ 25°C	pH	ALM 20	8.41	8.19	8.74	8.46	7.72	8.41	8.28
A	Electrical conductivity (EC) @ 25°C	mS/m	ALM 20	56.0	71.5	67.1	71.9	60.1	55.1	57.1
A	Total dissolved solids (TDS)	mg/l	ALM 26	317	424	367	418	327	307	327
A	Total alkalinity	mg CaCO3/l	ALM 01	205	198	223	209	287	200	209
A	Chloride (Cl)	mg/l	ALM 02	20.7	34.6	35.7	37.6	2.84	18.9	20.1
A	Sulphate (SO_4)	mg/l	ALM 03	29.6	32.7	32.8	36.9	34.9	25.4	32.8
A	Nitrate (NO_3) as N	mg/l	ALM 06	8.80	26.8	12.2	22.5	<0.194	9.35	9.54
A	Ammonium (NH_4) as N	mg/l	ALM 05	0.048	0.304	0.024	0.023	3.95	0.072	0.019
A	Orthophosphate (PO_4) as P	mg/l	ALM 04	0.106	0.044	0.116	0.039	0.048	0.045	0.043
A	Fluoride (F)	mg/l	ALM 08	<0.263	0.321	0.265	<0.263	0.326	<0.263	<0.263
A	Calcium (Ca)	mg/l	ALM 30	46.8	33.3	10.3	24.3	61.6	48.0	48.0
A	Magnesium (Mg)	mg/l	ALM 30	40.9	63.5	75.8	69.9	41.6	36.8	41.5
A	Sodium (Na)	mg/l	ALM 30	14.1	18.4	19.6	19.7	2.83	13.8	14.1
A	Potassium (K)	mg/l	ALM 30	0.718	1.86	2.15	2.22	2.28	0.696	0.761
A	Total hardness	mg CaCO3/l	ALM 26	285	345	338	349	325	271	291
N	Bromide (Br)	mg/l	ALM 70	0.260	<0.010	0.500	<0.010	<0.010	0.320	0.320

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Test Report

Client: University Of Pretoria
Address: Cnr Lynwood & Roper Roads, Hatfield, Pretoria, 0028
Report no: 45654
Project: University of Pretoria

Date of certificate: 06 November 2019
Date accepted: 17 October 2017
Date completed: 24 October 2017
Date received: 17 October 2017

Lab no:				84823	84824	84825
Date sampled:				18-Sep-17	18-Sep-17	18-Sep-17
Aquatico sampled:				Yes	Yes	Yes
Sample type:				Water	Water	Water
Locality description:				Fish Dam (FD)	September Blank	Slurry Dam (SyD) D
	Analyses	**Unit**	**Method**			
A	pH @ 25°C	pH	ALM 20	8.37	6.54	7.92
A	Electrical conductivity (EC) @ 25°C	mS/m	ALM 20	55.8	1.13	70.8
A	Total dissolved solids (TDS)	mg/l	ALM 26	320	<10	423
A	Total alkalinity	mg CaCO3/l	ALM 01	207	<1.99	185
A	Chloride (Cl)	mg/l	ALM 02	20.1	0.589	34.0
A	Sulphate (SO_4)	mg/l	ALM 03	29.7	<0.141	33.1
A	Nitrate (NO_3) as N	mg/l	ALM 06	9.02	0.416	28.1
A	Ammonium (NH_4) as N	mg/l	ALM 05	0.019	0.014	0.017
A	Orthophosphate (PO_4) as P	mg/l	ALM 04	0.041	0.042	0.045
A	Fluoride (F)	mg/l	ALM 08	0.292	<0.263	<0.263
A	Calcium (Ca)	mg/l	ALM 30	47.4	<0.082	33.4
A	Magnesium (Mg)	mg/l	ALM 30	41.3	<0.077	64.5
A	Sodium (Na)	mg/l	ALM 30	14.2	0.103	18.6
A	Potassium (K)	mg/l	ALM 30	0.776	0.085	1.82
A	Total hardness	mg CaCO3/l	ALM 26	288	0	349
N	Bromide (Br)	mg/l	ALM 70	0.350	0.040	0.480

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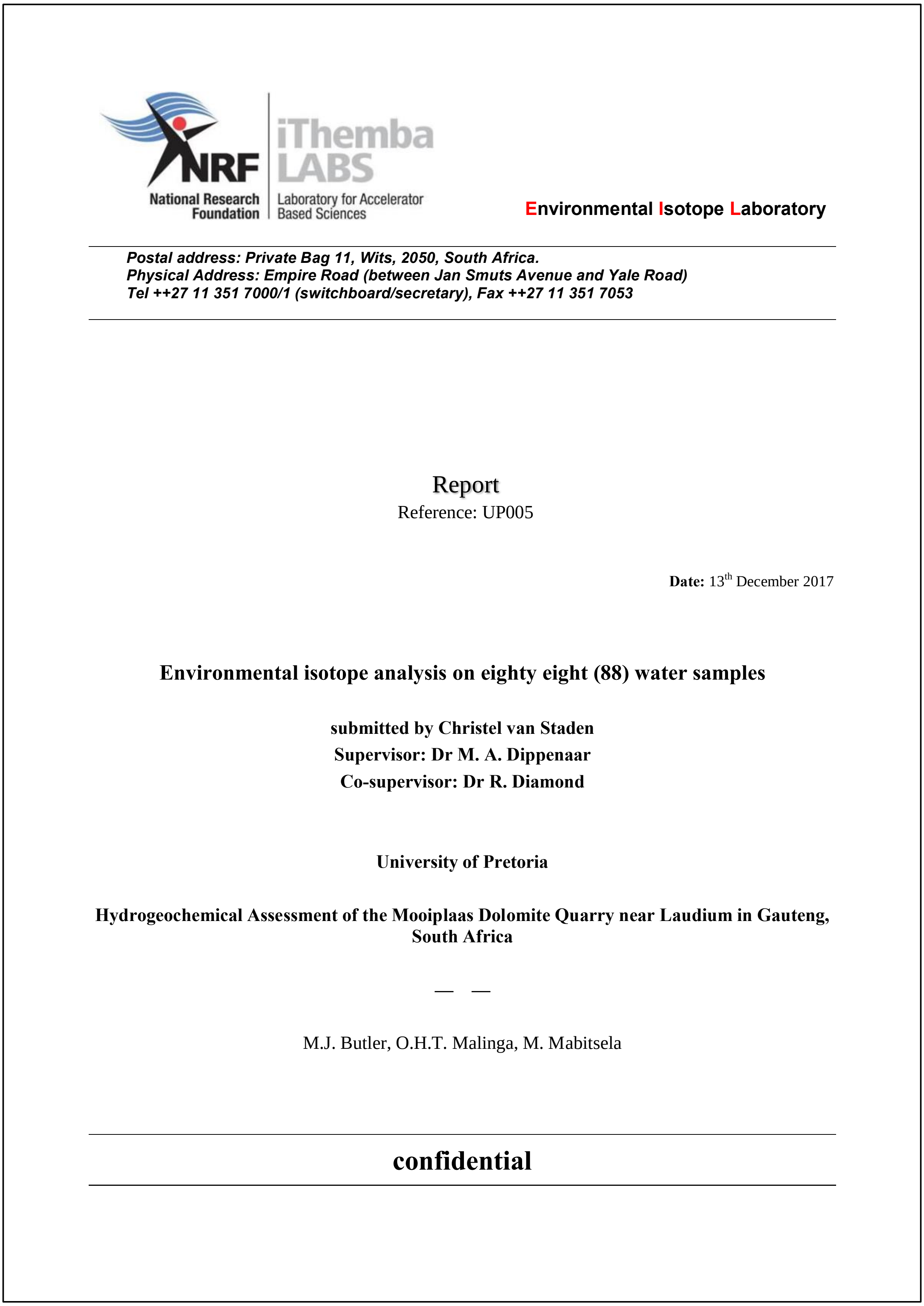
Appendix E: Isotope laboratory results

December 2017: Report reference UP005



NRF
National Research Foundation

iThemba LABS
Laboratory for Accelerator Based Sciences

Environmental Isotope Laboratory

Postal address: Private Bag 11, Wits, 2050, South Africa.
Physical Address: Empire Road (between Jan Smuts Avenue and Yale Road)
Tel ++27 11 351 7000/1 (switchboard/secretary), Fax ++27 11 351 7053

Report

Reference: UP005

Date: 13th December 2017

Environmental isotope analysis on eighty eight (88) water samples

submitted by Christel van Staden
Supervisor: Dr M. A. Dippenaar
Co-supervisor: Dr R. Diamond

University of Pretoria

Hydrogeochemical Assessment of the Mooiplaas Dolomite Quarry near Laudium in Gauteng, South Africa

— —

M.J. Butler, O.H.T. Malinga, M. Mabitsela

confidential

1. General

Eighty eight water samples were submitted by C. van Staden of the University of Pretoria for D/H ($^2H/^1H$) and $^{18}O/^{16}O$ analysis. The samples were received on the 4th of December 2017.

2. Stable Isotope Analysis

Water D/H ($^2H/^1H$) and $^{18}O/^{16}O$ ratios were analysed in the laboratory of the Environmental Isotope Group (EIG) of iThemba Laboratories, Gauteng.

The equipment used for stable isotope analysis consists of a Los Gatos Research (LGR) Liquid Water Isotope Analyser. Laboratory standards, calibrated against international reference materials, are analysed with each batch of samples. The analytical precision is estimated at 0.5‰ for O and 1.5‰ for H.

Analytical results are presented in the common delta-notation:

$$\delta^{18}O(‰) = \left[\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{standard}} - 1 \right] \times 1000$$

which applies to D/H ($^2H/^1H$), accordingly. These delta values are expressed as per mil deviation relative to a known standard, in this case standard mean ocean water (SMOW) for $\delta^{18}O$ and δD.

3. Results

The analytical results are presented in Tables 1 and 2 and partially illustrated in Figure 1.

The stable isotope analyses for all samples data could be well reproduced within the expected analytical error limits. Figure 1 shows these data in a $\delta^{18}O$ vs. δD space relative to the Global Meteoric Water Line (GMWL, Craig, 1961).

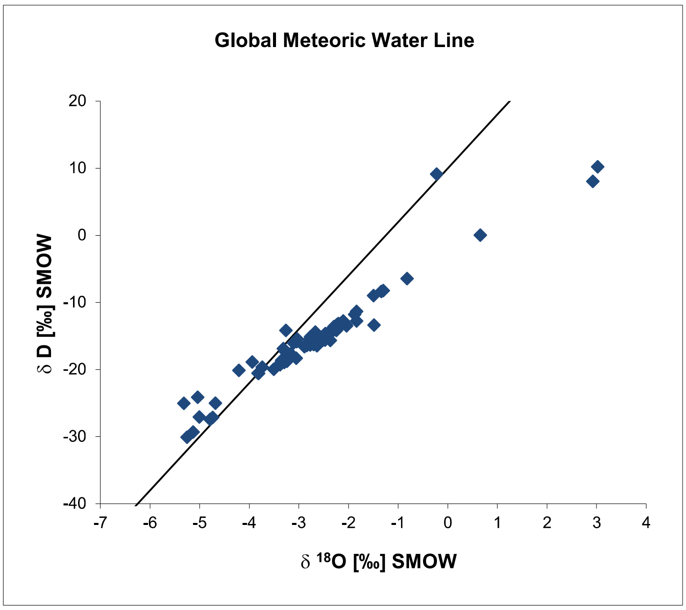


Figure 1: Stable isotope data relative to Global Meteoric Water Line (Craig, 1961).

4. References

Craig, H. (1961). Isotopic variations in meteoric waters. *Science*, **133**, 1702–1703.

Table 1: Analytical Results

		Deuterium	Oxygen-18
Lab No	**Field Name**	**δD‰ SMOW**	**δ^{18}O‰ SMOW**
UP 984	Plant Inlet (PI) - April	-15.7	-2.47
UP 985	Slurry Dam (SyD) - April	-14.5	-2.39
UP 986	MDV Slurry Dam (MDV SyD) – April	-13.6	-2.29
UP 987	Slimes Dam (SsD) - April	-13.5	-2.04
UP 988	West Pit Seep (WPS) - April	-20.6	-3.81
UP 989	West Pit (WP) – April	-19.0	-3.36
UP 990	Exploration Borehole North (Expl BH N) – April	-24.2	-5.04
UP 991	Exploration Borehole South (Expl BH S) – April	-30.1	-5.25
UP 992	Stream Outside – April	-17.7	-3.16
UP 993	Fish Dam (FD) – April	-14.9	-2.62
UP 994	Plant Inlet (PI) – May	-15.6	-2.74
UP 995	Slurry Dam (SyD) – May	-15.1	-2.75
UP 996	MDV Slurry Dam (MDV SyD) – May	-13.2	-2.20
UP 997	Slimes Dam (SsD) – May	+8.0	+2.93
UP 998	West Pit Seep (WPS) – May	-20.6	-3.82
UP 999	West Pit (WP) – May	-18.7	-3.34
UP 1000	West Pit Wall Seep (WPWS) – May	-15.7	-2.36
UP 1001	East Pit (EP) – May	-16.1	-2.75
UP 1002	Exploration Borehole North (Expl BH N) – May	-25.1	-5.31
UP 1003	Exploration Borehole South (Expl BH S) – May	-29.4	-5.13
UP 1004	Outside Stream – May	-15.6	-2.54
UP 1005	Fish Dam (FD) – May	-15.8	-2.52
UP 1006	Fish Dam (FD) D – May	-15.6	-2.79
UP 1007	Groundwater Flow 1 (GWF1) - April	-17.4	-3.27
UP 1008	Groundwater Flow 12 (GWF12) - April	-16.1	-3.11
UP 1009	Groundwater Flow 1 (GWF1) - May	-16.9	-3.31
UP 1010	Groundwater Flow 12 (GWF12) - May	-15.5	-3.03
UP 1011	December 2016 Rain	-20.2	-4.21
UP 1012	January 2017 Rain	-18.9	-3.94
UP 1013	February 2017 Rain	+9.1	-0.22
UP 1014	21 February 2017 Rain	-25.1	-4.68
UP 1015	March 2017 Rain	-14.6	-2.67
UP 1016	April 2017 Rain	-14.2	-3.26
UP 1017	May 2017 Rain	-72.0	-9.88
UP 1018	May 2017 Rain D	-72.6	-9.92
UP 1019	Plant Inlet (PI) - June	-16.5	-2.63
UP 1020	Slurry Dam (SyD) - June	-14.9	-2.40
UP 1021	MDV Slurry Dam (MDV SyD) - June	-12.8	-2.10
UP 1022	Slimes Dam (SsD) - June	+10.2	+3.02
UP 1023	West Pit Seep (WPS) - June	-17.9	-3.19
UP 1024	West Pit (WP) - June	-17.8	-3.16
UP 1025	West Pit Wall Seep (WPWS) - June	-14.2	-2.24
UP 1026	East Pit Wall Seep (EPWS) - June	-8.4	-1.34
UP 1027	East Pit (EP) - June	-15.9	-2.67
UP 1028	Fish Dam (FD) - June	-15.6	-2.66

UP 1029	West Pit Wall Seep (WPWS) D- June	-14.1	-2.27
UP 1030	Plant Inlet (PI) - July	-15.6	-2.68
UP 1031	Slurry Dam (SyD) - July	-14.7	-2.46
UP 1032	MDV Slurry Dam (SyD) - July	-14.6	-2.37
UP 1033	Slimes Dam (SsD) - July	-14.2	-2.33
UP 1034	West Pit (WP) - July	-18.7	-3.27
UP 1035	West Pit Wall Seep (WPWS) - July	-13.9	-2.20
UP 1036	East Pit Wall Seep (EPWS) - July	-9.1	-1.49
UP 1037	East Pit (EP) - July	-16.0	-2.70
UP 1038	Fish Dam (FD) - July	-15.6	-2.58
UP 1039	Plant Inlet (PI) D - July	-16.0	-2.67
UP 1040	Groundwater Flow 1 (GWF1) - June	-16.2	-2.74
UP 1041	Groundwater Flow 12 (GWF12) - June	-18.8	-3.24
UP 1042	Groundwater Flow 1 (GWF1) - July	-16.4	-2.77
UP 1043	Groundwater Flow 12 (GWF12) - July	-15.5	-2.55
UP 1044	Plant Inlet (PI) - August	-13.4	-1.48
UP 1045	Slurry Dam (SyD) - August	-11.8	-1.87
UP 1046	MDV Slurry Dam (MDV SyD) - August	-0.0	+0.66
UP 1047	Slimes Dam (SsD) - August	-20.0	-3.50
UP 1048	West Pit (WP) - August	-12.8	-1.83
UP 1049	West Pit Wall Seep (WPWS) - August	-8.3	-1.30
UP 1050	East Pit Wall Seep (EPWS) - August	-15.5	-2.58
UP 1051	East Pit (EP) - August	-15.2	-2.76
UP 1052	Fish Dam (FD) - August	-19.7	-3.74
UP 1053	West Pit (WP) D - August	-15.9	-3.04
UP 1054	Groundwater Flow 1 (GWF1) - August	-16.3	-2.70
UP 1055	Groundwater Flow 12 (GWF12) - August	-27.1	-5.00
UP 1056	Groundwater Flow 12 (GWF12) D - August	-14.5	-2.66
UP 1057	Plant Inlet (PI) - September	-13.4	-2.23
UP 1058	Slurry Dam (SyD) - September	-11.4	-1.83
UP 1059	MDV Slurry Dam (MDV SyD)- September	-6.5	-0.82
UP 1060	Slimes Dam (SsD) - September	-16.6	-2.89
UP 1061	West Pit (WP) - September	-14.9	-2.49
UP 1062	East Pit (EP) - September	-14.8	-2.43
UP 1063	Fish Dam (FD) - September	-13.4	-2.05
UP 1064	Slurry Dam (SyD) D - September	-18.3	-3.05
UP 1065	Groundwater Flow 1 (GWF1) - September	-16.4	-2.62
UP 1066	Groundwater Flow 12 (GWF12) - September	-19.3	-3.37
UP 1067	Groundwater Flow 1 (GWF1) D - September	-19.0	-3.29
UP 1068	Groundwater Flow 1 (GWF1) D - September	-16.5	-2.84
UP 1069	Groundwater Flow 12 (GWF12) D - September	-16.4	-2.84
UP 1070	Groundwater Flow 12 (GWF12) D - September	-27.5	-4.79
UP 1071	Exploration Borehole South (Expl BH S) - September	-27.2	-4.73

Table 2: Stable isotope aliquot determinations

		Deuterium			Oxygen-18		
Lab No.	Field Name:	analysis	Batch	δD‰ **SMOW**	analysis	Batch	δ^{18}O‰ **SMOW**
UP 984	Plant Inlet (PI) - April	a	2017/12/08	-16.1	a	2017/12/08	-2.51
		b		-15.2	b		-2.43
			avg.:	**-15.7**		**avg.:**	**-2.47**
			diff.:	*1.0*		*diff.:*	*0.08*
UP 985	Slurry Dam (SyD) - April	a	2017/12/08	-14.5	a	2017/12/08	-2.38
		b		-14.5	b		-2.40
			avg.:	**-14.5**		**avg.:**	**-2.39**
			diff.:	*0.0*		*diff.:*	*0.02*
UP 986	MDV Slurry Dam (MDV SyD) – April	a	2017/12/08	-13.8	a	2017/12/08	-2.25
		b		-13.5	b		-2.32
			avg.:	**-13.6**		**avg.:**	**-2.29**
			diff.:	*0.3*		*diff.:*	*0.07*
UP 987	Slimes Dam (SsD) - April	a	2017/12/08	-13.6	a	2017/12/08	-2.05
		b		-13.5	b		-2.02
			avg.:	**-13.5**		**avg.:**	**-2.04**
			diff.:	*0.0*		*diff.:*	*0.03*
UP 988	West Pit Seep (WPS) - April	a	2017/12/08	-20.4	a	2017/12/08	-3.75
		b		-20.9	b		-3.87
			avg.:	**-20.6**		**avg.:**	**-3.81**
			diff.:	*0.4*		*diff.:*	*0.11*
UP 989	West Pit (WP) – April	a	2017/12/08	-18.9	a	2017/12/08	-3.32
		b		-19.1	b		-3.39
			avg.:	**-19.0**		**avg.:**	**-3.36**
			diff.:	*0.2*		*diff.:*	*0.06*
UP 990	Exploration Borehole North (Expl BH N) – April	a	2017/12/08	-23.7	a	2017/12/08	-4.98
		b		-24.7	b		-5.09
			avg.:	**-24.2**		**avg.:**	**-5.04**
			diff.:	*1.0*		*diff.:*	*0.10*
UP 991	Exploration Borehole South (Expl BH S) – April	a	2017/12/08	-30.2	a	2017/12/08	-5.28
		b		-30.1	b		-5.22
			avg.:	**-30.1**		**avg.:**	**-5.25**
			diff.:	*0.1*		*diff.:*	*0.06*
UP 992	Stream Outside – April	a	2017/12/08	-17.5	a	2017/12/08	-3.14
		b		-17.9	b		-3.18
			avg.:	**-17.7**		**avg.:**	**-3.16**
			diff.:	*0.3*		*diff.:*	*0.03*
UP 993	Fish Dam (FD) – April	a	2017/12/08	-14.9	a	2017/12/08	-2.65
		b		-14.8	b		-2.59
			avg.:	**-14.9**		**avg.:**	**-2.62**
			diff.:	*0.2*		*diff.:*	*0.06*
UP 994	Plant Inlet (PI) – May	a	2017/12/08	-15.4	a	2017/12/08	-2.76
		b		-15.7	b		-2.73
			avg.:	**-15.6**		**avg.:**	**-2.74**
			diff.:	*0.3*		*diff.:*	*0.03*
UP 995	Slurry Dam (SyD) – May	a	2017/12/08	-15.1	a	2017/12/08	-2.73
		b		-15.2	b		-2.76
			avg.:	**-15.1**		**avg.:**	**-2.75**
			diff.:	*0.1*		*diff.:*	*0.02*
UP 996	MDV Slurry Dam (MDV SyD) – May	a	2017/12/08	-13.5	a	2017/12/08	-2.27
		b		-12.9	b		-2.13
			avg.:	**-13.2**		**avg.:**	**-2.20**
			diff.:	*0.6*		*diff.:*	*0.14*
UP 997	Slimes Dam (SsD) – May	a	2017/12/08	8.2	a	2017/12/08	2.88
		b		7.8	b		2.98
			avg.:	**8.0**		**avg.:**	**2.93**
			diff.:	*0.3*		*diff.:*	*0.10*

UP 998	West Pit Seep (WPS) – May	a	2017/12/08	-20.4	a	2017/12/08	-3.83
		b		-20.8	b		-3.81
			avg.:	**-20.6**		**avg.:**	**-3.82**
			diff.:	*0.4*		*diff.:*	*0.02*
UP 999	West Pit (WP) – May	a	2017/12/08	-18.6	a	2017/12/08	-3.33
		b		-18.7	b		-3.36
			avg.:	**-18.7**		**avg.:**	**-3.34**
			diff.:	*0.1*		*diff.:*	*0.03*
UP 1000	West Pit Wall Seep (WPWS) – May	a	2017/12/08	-16.1	a	2017/12/08	-2.38
		b		-15.4	b		-2.34
			avg.:	**-15.7**		**avg.:**	**-2.36**
			diff.:	*0.7*		*diff.:*	*0.05*
UP 1001	East Pit (EP) – May	a	2017/12/08	-16.2	a	2017/12/08	-2.75
		b		-15.9	b		-2.75
			avg.:	**-16.1**		**avg.:**	**-2.75**
			diff.:	*0.3*		*diff.:*	*0.01*
UP 1002	Exploration Borehole North (Expl BH N) – May	a	2017/12/08	-24.9	a	2017/12/08	-5.33
		b		-25.3	b		-5.30
			avg.:	**-25.1**		**avg.:**	**-5.31**
			diff.:	*0.3*		*diff.:*	*0.04*
UP 1003	Exploration Borehole South (Expl BH S) – May	a	2017/12/11	-29.4	a	2017/12/11	-5.11
		b		-29.4	b		-5.15
			avg.:	**-29.4**		**avg.:**	**-5.13**
			diff.:	*0.0*		*diff.:*	*0.03*
UP 1004	Outside Stream – May	a	2017/12/13	-15.8	a	2017/12/13	-2.54
		b		-15.3	b		-2.54
			avg.:	**-15.6**		**avg.:**	**-2.54**
			diff.:	*0.5*		*diff.:*	*0.00*
UP 1005	Fish Dam (FD) – May	a	2017/12/11	-15.8	a	2017/12/11	-2.52
		b		-15.7	b		-2.53
			avg.:	**-15.8**		**avg.:**	**-2.52**
			diff.:	*0.1*		*diff.:*	*0.02*
UP 1006	Fish Dam (FD) D – May	a	2017/12/11	-15.6	a	2017/12/11	-2.79
		b		-15.7	b		-2.78
			avg.:	**-15.6**		**avg.:**	**-2.79**
			diff.:	*0.1*		*diff.:*	*0.02*
UP 1007	Groundwater Flow 1 (GWF1) - April	a	2017/12/11	-17.3	a	2017/12/11	-3.30
		b		-17.5	b		-3.23
			avg.:	**-17.4**		**avg.:**	**-3.27**
			diff.:	*0.1*		*diff.:*	*0.07*
UP 1008	Groundwater Flow 12 (GWF12) - April	a	2017/12/11	-16.2	a	2017/12/11	-3.15
		b		-16.1	b		-3.07
			avg.:	**-16.1**		**avg.:**	**-3.11**
			diff.:	*0.1*		*diff.:*	*0.08*
UP 1009	Groundwater Flow 1 (GWF1) - May	a	2017/12/11	-16.9	a	2017/12/11	-3.33
		b		-17.0	b		-3.30
			avg.:	**-16.9**		**avg.:**	**-3.31**
			diff.:	*0.1*		*diff.:*	*0.03*
UP 1010	Groundwater Flow 12 (GWF12) - May	a	2017/12/11	-15.5	a	2017/12/11	-3.03
		b		-15.5	b		-3.04
			avg.:	**-15.5**		**avg.:**	**-3.03**
			diff.:	*0.0*		*diff.:*	*0.01*
UP 1011	December 2016 Rain	a	2017/12/11	-20.0	a	2017/12/11	-4.21
		b		-20.3	b		-4.20
			avg.:	**-20.2**		**avg.:**	**-4.21**
			diff.:	*0.3*		*diff.:*	*0.02*
UP 1012	January 2017 Rain	a	2017/12/11	-18.9	a	2017/12/11	-3.91
		b		-19.0	b		-3.96
			avg.:	**-18.9**		**avg.:**	**-3.94**
			diff.:	*0.1*		*diff.:*	*0.05*
UP 1013	February 2017 Rain	a	2017/12/11	8.9	a	2017/12/11	-0.24
		b		9.3	b		-0.20
			avg.:	**9.1**		**avg.:**	**-0.22**
			diff.:	*0.4*		*diff.:*	*0.05*

UP 1014	21 February 2017 Rain	a	2017/12/11	-24.8	a	2017/12/11	-4.71
		b		-25.3	b		-4.65
			avg.:	**-25.1**		**avg.:**	**-4.68**
			diff.:	*0.5*		*diff.:*	*0.06*
UP 1015	March 2017 Rain	a	2017/12/13	-14.9	a	2017/12/13	-2.70
		b		-14.4	b		-2.63
			avg.:	**-14.6**		**avg.:**	**-2.67**
			diff.:	*0.5*		*diff.:*	*0.08*
UP 1016	April 2017 Rain	a	2017/12/11	-14.1	a	2017/12/11	-3.26
		b		-14.3	b		-3.25
			avg.:	**-14.2**		**avg.:**	**-3.26**
			diff.:	*0.2*		*diff.:*	*0.01*
UP 1017	May 2017 Rain	a	2017/12/11	-71.7	a	2017/12/11	-9.89
		b		-72.4	b		-9.86
			avg.:	**-72.0**		**avg.:**	**-9.88**
			diff.:	*0.7*		*diff.:*	*0.04*
UP 1018	May 2017 Rain D	a	2017/12/11	-72.6	a	2017/12/11	-9.93
		b		-72.7	b		-9.91
			avg.:	**-72.6**		**avg.:**	**-9.92**
			diff.:	*0.2*		*diff.:*	*0.02*
UP 1019	Plant Inlet (PI) - June	a	2017/12/11	-16.8	a	2017/12/11	-2.69
		b		-16.2	b		-2.58
			avg.:	**-16.5**		**avg.:**	**-2.63**
			diff.:	*0.7*		*diff.:*	*0.11*
UP 1020	Slurry Dam (SyD) - June	a	2017/12/11	-14.9	a	2017/12/11	-2.40
		b		-14.8	b		-2.40
			avg.:	**-14.9**		**avg.:**	**-2.40**
			diff.:	*0.1*		*diff.:*	*0.01*
UP 1021	MDV Slurry Dam (MDV SyD) - June	a	2017/12/11	-12.7	a	2017/12/11	-2.10
		b		-12.9	b		-2.11
			avg.:	**-12.8**		**avg.:**	**-2.10**
			diff.:	*0.2*		*diff.:*	*0.01*
UP 1022	Slimes Dam (SsD) - June	a	2017/12/11	10.1	a	2017/12/11	3.02
		b		10.3	b		3.03
			avg.:	**10.2**		**avg.:**	**3.02**
			diff.:	*0.2*		*diff.:*	*0.01*
UP 1023	West Pit Seep (WPS) - June	a	2017/12/11	-17.7	a	2017/12/11	-3.17
		b		-18.2	b		-3.22
			avg.:	**-17.9**		**avg.:**	**-3.19**
			diff.:	*0.5*		*diff.:*	*0.05*
UP 1024	West Pit (WP) - June	a	2017/12/11	-17.8	a	2017/12/11	-3.17
		b		-17.8	b		-3.15
			avg.:	**-17.8**		**avg.:**	**-3.16**
			diff.:	*0.1*		*diff.:*	*0.02*
UP 1025	West Pit Wall Seep (WPWS) - June	a	2017/12/11	-14.2	a	2017/12/11	-2.24
		b		-14.2	b		-2.25
			avg.:	**-14.2**		**avg.:**	**-2.24**
			diff.:	*0.0*		*diff.:*	*0.01*
UP 1026	East Pit Wall Seep (EPWS) - June	a	2017/12/11	-8.4	a	2017/12/11	-1.34
		b		-8.5	b		-1.33
			avg.:	**-8.4**		**avg.:**	**-1.34**
			diff.:	*0.1*		*diff.:*	*0.01*
UP 1027	East Pit (EP) - June	a	2017/12/11	-15.8	a	2017/12/11	-2.64
		b		-16.0	b		-2.69
			avg.:	**-15.9**		**avg.:**	**-2.67**
			diff.:	*0.3*		*diff.:*	*0.05*
UP 1028	Fish Dam (FD) - June	a	2017/12/11	-15.6	a	2017/12/11	-2.66
		b		-15.6	b		-2.65
			avg.:	**-15.6**		**avg.:**	**-2.66**
			diff.:	*0.1*		*diff.:*	*0.01*
UP 1029	West Pit Wall Seep (WPWS) D- June	a	2017/12/11	-14.1	a	2017/12/11	-2.26
		b		-14.1	b		-2.29
			avg.:	**-14.1**		**avg.:**	**-2.27**
			diff.:	*0.1*		*diff.:*	*0.03*

UP 1030	Plant Inlet (PI) - July	a	2017/12/11	-15.5	a	2017/12/11	-2.69
		b		-15.6	b		-2.68
			avg.:	**-15.6**		**avg.:**	**-2.68**
			diff.:	*0.1*		*diff.:*	*0.01*
UP 1031	Slurry Dam (SyD) - July	a	2017/12/11	-14.7	a	2017/12/11	-2.49
		b		-14.7	b		-2.44
			avg.:	**-14.7**		**avg.:**	**-2.46**
			diff.:	*0.0*		*diff.:*	*0.06*
UP 1032	MDV Slurry Dam (SyD) - July	a	2017/12/11	-14.7	a	2017/12/11	-2.39
		b		-14.4	b		-2.36
			avg.:	**-14.6**		**avg.:**	**-2.37**
			diff.:	*0.3*		*diff.:*	*0.03*
UP 1033	Slimes Dam (SsD) - July	a	2017/12/11	-14.2	a	2017/12/11	-2.33
		b		-14.2	b		-2.34
			avg.:	**-14.2**		**avg.:**	**-2.33**
			diff.:	*0.0*		*diff.:*	*0.02*
UP 1034	West Pit (WP) - July	a	2017/12/11	-18.7	a	2017/12/11	-3.30
		b		-18.8	b		-3.23
			avg.:	**-18.7**		**avg.:**	**-3.27**
			diff.:	*0.0*		*diff.:*	*0.07*
UP 1035	West Pit Wall Seep (WPWS) - July	a	2017/12/11	-13.8	a	2017/12/11	-2.20
		b		-13.9	b		-2.20
			avg.:	**-13.9**		**avg.:**	**-2.20**
			diff.:	*0.1*		*diff.:*	*0.00*
UP 1036	East Pit Wall Seep (EPWS) - July	a	2017/12/11	-9.1	a	2017/12/11	-1.53
		b		-9.0	b		-1.45
			avg.:	**-9.1**		**avg.:**	**-1.49**
			diff.:	*0.0*		*diff.:*	*0.07*
UP 1037	East Pit (EP) - July	a	2017/12/11	-16.0	a	2017/12/11	-2.77
		b		-16.1	b		-2.64
			avg.:	**-16.0**		**avg.:**	**-2.70**
			diff.:	*0.1*		*diff.:*	*0.12*
UP 1038	Fish Dam (FD) - July	a	2017/12/11	-15.6	a	2017/12/11	-2.59
		b		-15.6	b		-2.57
			avg.:	**-15.6**		**avg.:**	**-2.58**
			diff.:	*0.0*		*diff.:*	*0.02*
UP 1039	Plant Inlet (PI) D - July	a	2017/12/11	-15.9	a	2017/12/11	-2.69
		b		-16.0	b		-2.66
			avg.:	**-16.0**		**avg.:**	**-2.67**
			diff.:	*0.1*		*diff.:*	*0.03*
UP 1040	Groundwater Flow 1 (GWF1) - June	a	2017/12/11	-16.3	a	2017/12/11	-2.76
		b		-16.2	b		-2.72
			avg.:	**-16.2**		**avg.:**	**-2.74**
			diff.:	*0.1*		*diff.:*	*0.03*
UP 1041	Groundwater Flow 12 (GWF12) - June	a	2017/12/11	-18.8	a	2017/12/11	-3.25
		b		-18.9	b		-3.22
			avg.:	**-18.8**		**avg.:**	**-3.24**
			diff.:	*0.1*		*diff.:*	*0.02*
UP 1042	Groundwater Flow 1 (GWF1) - July	a	2017/12/11	-16.4	a	2017/12/11	-2.82
		b		-16.4	b		-2.72
			avg.:	**-16.4**		**avg.:**	**-2.77**
			diff.:	*0.0*		*diff.:*	*0.10*
UP 1043	Groundwater Flow 12 (GWF12) - July	a	2017/12/11	-15.6	a	2017/12/11	-2.60
		b		-15.4	b		-2.50
			avg.:	**-15.5**		**avg.:**	**-2.55**
			diff.:	*0.1*		*diff.:*	*0.11*
UP 1044	Plant Inlet (PI) - August	a	2017/12/13	-13.5	a	2017/12/13	-1.54
		b		-13.3	b		-1.43
			avg.:	**-13.4**		**avg.:**	**-1.48**
			diff.:	*0.2*		*diff.:*	*0.11*
UP 1045	Slurry Dam (SyD) - August	a	2017/12/11	-11.8	a	2017/12/11	-1.90
		b		-11.8	b		-1.84
			avg.:	**-11.8**		**avg.:**	**-1.87**
			diff.:	*0.0*		*diff.:*	*0.06*

UP 1046	MDV Slurry Dam (MDV SyD) - August	a	2017/12/11	0.0	a	2017/12/11	0.65
		b		-0.1	b		0.67
			avg.:	**0.0**		**avg.:**	**0.66**
			diff.:	*0.1*		*diff.:*	*0.01*
UP 1047	Slimes Dam (SsD) - August	a	2017/12/11	-19.8	a	2017/12/11	-3.52
		b		-20.3	b		-3.48
			avg.:	**-20.0**		**avg.:**	**-3.50**
			diff.:	*0.5*		*diff.:*	*0.03*
UP 1048	West Pit (WP) - August	a	2017/12/11	-12.8	a	2017/12/11	-1.84
		b		-12.8	b		-1.82
			avg.:	**-12.8**		**avg.:**	**-1.83**
			diff.:	*0.0*		*diff.:*	*0.02*
UP 1049	West Pit Wall Seep (WPWS) - August	a	2017/12/11	-8.4	a	2017/12/11	-1.36
		b		-8.2	b		-1.23
			avg.:	**-8.3**		**avg.:**	**-1.30**
			diff.:	*0.2*		*diff.:*	*0.13*
UP 1050	East Pit Wall Seep (EPWS) - August	a	2017/12/11	-15.4	a	2017/12/11	-2.60
		b		-15.6	b		-2.56
			avg.:	**-15.5**		**avg.:**	**-2.58**
			diff.:	*0.2*		*diff.:*	*0.04*
UP 1051	East Pit (EP) - August	a	2017/12/11	-15.0	a	2017/12/11	-2.74
		b		-15.3	b		-2.79
			avg.:	**-15.2**		**avg.:**	**-2.76**
			diff.:	*0.3*		*diff.:*	*0.05*
UP 1052	Fish Dam (FD) - August	a	2017/12/11	-19.7	a	2017/12/11	-3.78
		b		-19.7	b		-3.70
			avg.:	**-19.7**		**avg.:**	**-3.74**
			diff.:	*0.1*		*diff.:*	*0.08*
UP 1053	West Pit (WP) D - August	a	2017/12/11	-15.9	a	2017/12/11	-3.10
		b		-15.8	b		-2.98
			avg.:	**-15.9**		**avg.:**	**-3.04**
			diff.:	*0.1*		*diff.:*	*0.12*
UP 1054	Groundwater Flow 1 (GWF1) - August	a	2017/12/13	-16.5	a	2017/12/13	-2.76
		b		-16.1	b		-2.64
			avg.:	**-16.3**		**avg.:**	**-2.70**
			diff.:	*0.3*		*diff.:*	*0.11*
UP 1055	Groundwater Flow 12 (GWF12) - August	a	2017/12/11	-27.1	a	2017/12/11	-5.03
		b		-27.1	b		-4.98
			avg.:	**-27.1**		**avg.:**	**-5.00**
			diff.:	*0.1*		*diff.:*	*0.05*
UP 1056	Groundwater Flow 12 (GWF12) D - August	a	2017/12/11	-14.4	a	2017/12/11	-2.68
		b		-14.6	b		-2.65
			avg.:	**-14.5**		**avg.:**	**-2.66**
			diff.:	*0.2*		*diff.:*	*0.04*
UP 1057	Plant Inlet (PI) - September	a	2017/12/11	-13.3	a	2017/12/11	-2.22
		b		-13.4	b		-2.25
			avg.:	**-13.4**		**avg.:**	**-2.23**
			diff.:	*0.1*		*diff.:*	*0.03*
UP 1058	Slurry Dam (SyD) - September	a	2017/12/13	-11.5	a	2017/12/13	-1.82
		b		-11.3	b		-1.84
			avg.:	**-11.4**		**avg.:**	**-1.83**
			diff.:	*0.1*		*diff.:*	*0.02*
UP 1059	MDV Slurry Dam (MDV SyD)- September	a	2017/12/13	-6.6	a	2017/12/13	-0.79
		b		-6.4	b		-0.85
			avg.:	**-6.5**		**avg.:**	**-0.82**
			diff.:	*0.3*		*diff.:*	*0.06*
UP 1060	Slimes Dam (SsD) - September	a	2017/12/11	-16.5	a	2017/12/11	-2.85
		b		-16.8	b		-2.92
			avg.:	**-16.6**		**avg.:**	**-2.89**
			diff.:	*0.3*		*diff.:*	*0.07*
UP 1061	West Pit (WP) - September	a	2017/12/11	-14.8	a	2017/12/11	-2.49
		b		-15.0	b		-2.50
			avg.:	**-14.9**		**avg.:**	**-2.49**
			diff.:	*0.2*		*diff.:*	*0.01*

UP 1062	East Pit (EP) - September	a	2017/12/11	-14.8	a	2017/12/11	-2.47
		b		-14.7	b		-2.39
			avg.:	**-14.8**		**avg.:**	**-2.43**
			diff.:	*0.1*		*diff.:*	*0.08*
UP 1063	Fish Dam (FD) - September	a	2017/12/11	-13.3	a	2017/12/11	-2.05
		b		-13.5	b		-2.05
			avg.:	**-13.4**		**avg.:**	**-2.05**
			diff.:	*0.2*		*diff.:*	*0.01*
UP 1064	Slurry Dam (SyD) D - September	a	2017/12/11	-18.2	a	2017/12/11	-3.02
		b		-18.5	b		-3.09
			avg.:	**-18.3**		**avg.:**	**-3.05**
			diff.:	*0.2*		*diff.:*	*0.07*
UP 1065	Groundwater Flow 1 (GWF1) - September	a	2017/12/11	-16.4	a	2017/12/11	-2.62
		b		-16.4	b		-2.62
			avg.:	**-16.4**		**avg.:**	**-2.62**
			diff.:	*0.0*		*diff.:*	*0.00*
UP 1066	Groundwater Flow 12 (GWF12) - September	a	2017/12/11	-19.1	a	2017/12/11	-3.41
		b		-19.6	b		-3.34
			avg.:	**-19.3**		**avg.:**	**-3.37**
			diff.:	*0.4*		*diff.:*	*0.07*
UP 1067	Groundwater Flow 1 (GWF1) D - September	a	2017/12/11	-19.0	a	2017/12/11	-3.30
		b		-19.1	b		-3.28
			avg.:	**-19.0**		**avg.:**	**-3.29**
			diff.:	*0.1*		*diff.:*	*0.02*
UP 1068	Groundwater Flow 1 (GWF1) D - September	a	2017/12/11	-16.5	a	2017/12/11	-2.80
		b		-16.4	b		-2.87
			avg.:	**-16.5**		**avg.:**	**-2.84**
			diff.:	*0.0*		*diff.:*	*0.08*
UP 1069	Groundwater Flow 12 (GWF12) D - September	a	2017/12/11	-16.4	a	2017/12/11	-2.84
		b		-16.5	b		-2.84
			avg.:	**-16.4**		**avg.:**	**-2.84**
			diff.:	*0.1*		*diff.:*	*0.00*
UP 1070	Groundwater Flow 12 (GWF12) D - September	a	2017/12/11	-27.4	a	2017/12/11	-4.75
		b		-27.5	b		-4.83
			avg.:	**-27.5**		**avg.:**	**-4.79**
			diff.:	*0.1*		*diff.:*	*0.07*
UP 1071	Exploration Borehole South (Expl BH S) - September	a	2017/12/11	-27.2	a	2017/12/11	-4.73
		b		-27.2	b		-4.74
			avg.:	**-27.2**		**avg.:**	**-4.73**
			diff.:	*0.1*		*diff.:*	*0.01*

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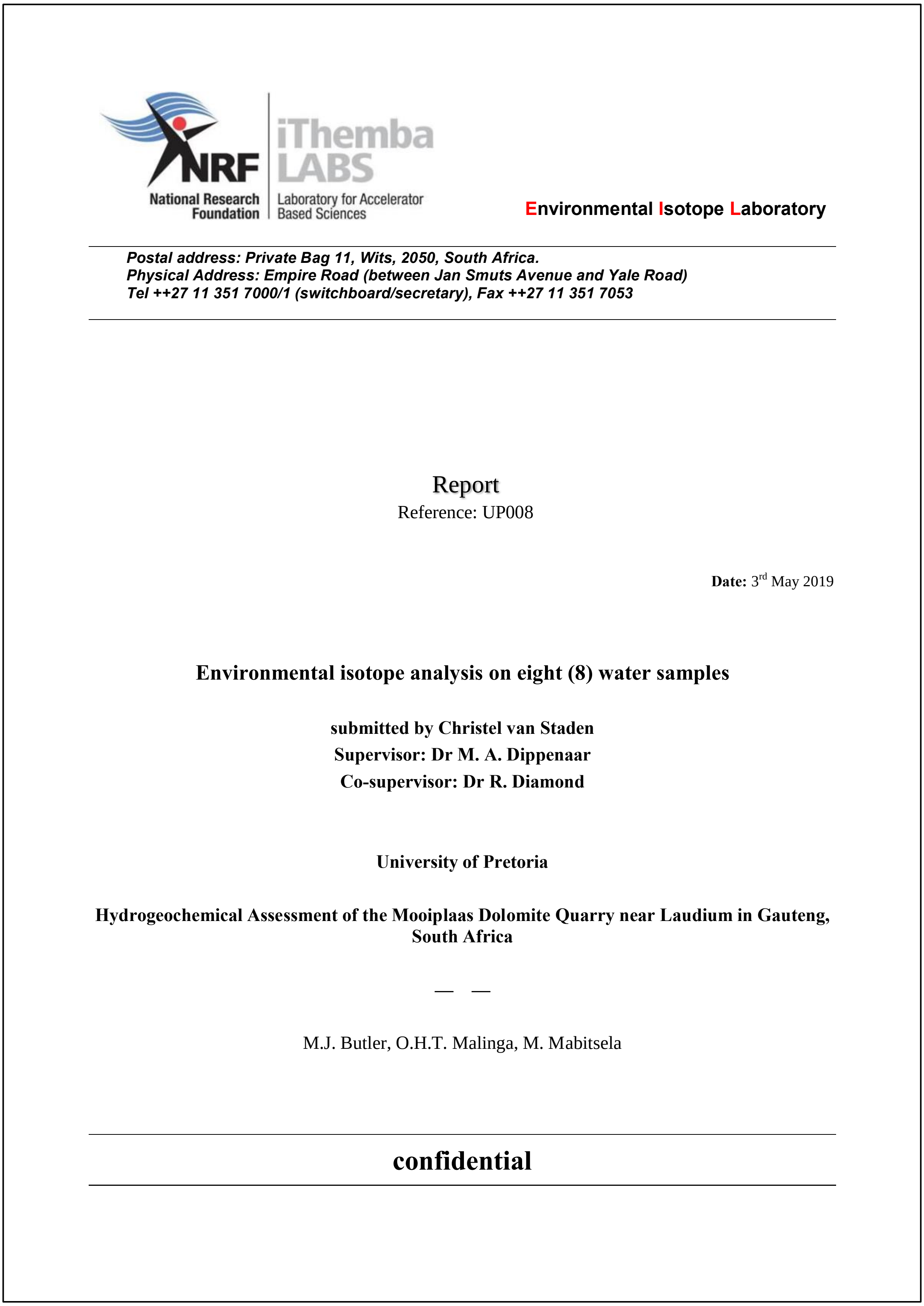

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Report

Reference: UP008

Date: 3rd May 2019

Environmental isotope analysis on eight (8) water samples

submitted by Christel van Staden
Supervisor: Dr M. A. Dippenaar
Co-supervisor: Dr R. Diamond

University of Pretoria

Hydrogeochemical Assessment of the Mooiplaas Dolomite Quarry near Laudium in Gauteng, South Africa

— —

M.J. Butler, O.H.T. Malinga, M. Mabitsela

confidential

1. General

Eight water samples were submitted by C. van Staden of the University of Pretoria for D/H ($^2H/^1H$) and $^{18}O/^{16}O$ analysis. The samples were received on the 23rd of January 2019.

2. Stable Isotope Analysis

Water D/H (2H/1H) and 18O/16O ratios were analysed in the laboratory of the Environmental Isotope Laboratory (EIL) of iThemba LABS, Johannesburg.

The equipment used for stable isotope analysis consists of a Los Gatos Research (LGR) Liquid Water Isotope Analyser. Laboratory standards, calibrated against international reference materials, are analysed with each batch of samples. The analytical precision is estimated at 0.5‰ for O and 1.5‰ for H.

Analytical results are presented in the common delta-notation:

$$\delta^{18}O(‰) = \left[\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{standard}} - 1 \right] \times 1000$$

which applies to D/H ($^2H/^1H$), accordingly. These delta values are expressed as per mil deviation relative to a known standard, in this case standard mean ocean water (SMOW) for $\delta^{18}O$ and δD.

3. Results

The analytical results are presented in Tables 1 and 2 and partially illustrated in Figure 1.

The stable isotope analyses for all samples data could be well reproduced within the expected analytical error limits. Figure 1 shows these data in a $\delta^{18}O$ vs. δD space relative to the Global Meteoric Water Line (GMWL, Craig, 1961).

4. References

Craig, H. (1961). Isotopic variations in meteoric waters. *Science*, **133**, 1702–1703.

Table 1: Analytical Results

		Deuterium	Oxygen-18
Lab No	Field Name	δD‰ SMOW	δ^{18}O‰ SMOW
UP 1106	December 2017 Rain	-22.3	-5.18
UP 1107	January 2018 Rain	+4.8	-0.72
UP 1108	February 2018 Rain	-5.5	-1.97
UP 1109	22 March 2018 Rain	-22.6	-4.96
UP 1110	23 March 2018 Rain	-34.5	-6.28
UP 1111	March 2018 Rain	-23.0	-4.72
UP 1112	April 2018 Rain	-32.0	-5.83
UP 1113	May 2018 Rain	+40.2	+3.54

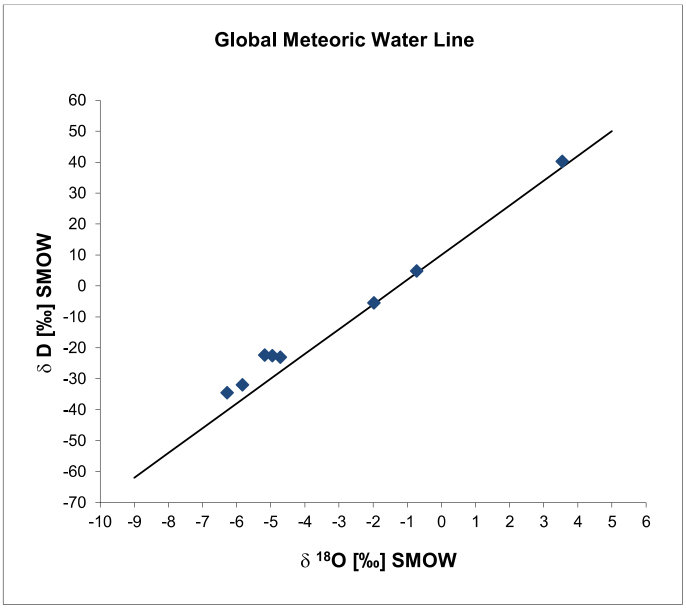

Figure 1: Stable isotope data relative to Global Meteoric Water Line (Craig, 1961).

Table 2: Stable isotope aliquot determinations

		Deuterium			Oxygen-18		
Lab No.	Field Name:	analysis	Batch	**δD‰ SMOW**	analysis	Batch	**δ^{18}O‰ SMOW**
UP 1106	December 2017 Rain	a	2019/01/24	-22.3	a	2019/01/24	-5.13
		b		-22.3	b		-5.22
			avg.:	**-22.3**		**avg.:**	**-5.18**
			diff.:	*0.0*		*diff.:*	*0.08*
UP 1107	January 2018 Rain	a	2019/01/24	4.7	a	2019/01/24	-0.73
		b		4.9	b		-0.71
			avg.:	**4.8**		**avg.:**	**-0.72**
			diff.:	*0.1*		*diff.:*	*0.02*
UP 1108	February 2018 Rain	a	2019/01/24	-5.1	a	2019/01/24	-1.96
		b		-5.8	b		-1.99
			avg.:	**-5.5**		**avg.:**	**-1.97**
			diff.:	*0.7*		*diff.:*	*0.03*
UP 1109	22 March 2018 Rain	a	2019/01/24	-22.5	a	2019/01/24	-5.01
		b		-22.7	b		-4.90
			avg.:	**-22.6**		**avg.:**	**-4.96**
			diff.:	*0.2*		*diff.:*	*0.12*
UP 1110	23 March 2018 Rain	a	2019/01/24	-34.7	a	2019/01/24	-6.33
		b		-34.2	b		-6.23
			avg.:	**-34.5**		**avg.:**	**-6.28**
			diff.:	*0.5*		*diff.:*	*0.10*
UP 1111	March 2018 Rain	a	2019/01/24	-23.1	a	2019/01/24	-4.75
		b		-22.9	b		-4.69
			avg.:	**-23.0**		**avg.:**	**-4.72**
			diff.:	*0.2*		*diff.:*	*0.05*
UP 1112	April 2018 Rain	a	2019/01/24	-31.8	a	2019/01/24	-5.80
		b		-32.2	b		-5.86
			avg.:	**-32.0**		**avg.:**	**-5.83**
			diff.:	*0.3*		*diff.:*	*0.06*
UP 1113	May 2018 Rain	a	2019/01/24	39.8	a	2019/01/24	3.50
		b		40.7	b		3.58
			avg.:	**40.2**		**avg.:**	**3.54**
			diff.:	*0.9*		*diff.:*	*0.08*

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