The use of constructed wetlands to ameliorate discharge water from coal mines in the Witbank Coalfield

By

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DECLARATION

I declare the thesis titled “The use of constructed wetlands to ameliorate discharge water from Coal mines in the Witbank coalfield” is my research work, that it has not been submitted before for any degree or examination in any other university, and that all the sources I have used or cited have been indicated and acknowledged by complete references.

Signed: …………………………….. **Date: ……………………………..**

DEDICATION

I dedicate my work to my family and many friends. A special feeling of gratitude to my loving parents, Phineas and Winnie Mahlase for their wise counsel and sympathetic ear, my husband who has always believed in me and has never left my side.

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ABSTRACT

Mining has a lengthy history in South Africa, and subsequent beneficiation processes have been conducted with little regard for the environment, thus leaving the land with un-rehabilitated abandoned mines. Currently, most of these abandoned mine sites are no longer operational and they continuously contaminate soil, air and water resources in various areas where mining took place. This study looks at the treatment of contaminated mine water using the Dispersed Alkaline Substrates (DAS) which is a new South African technology that uses a variety of substrates to neutralize and raise the pH of mine water while lowering the solubility of potentially dangerous metals.

The purpose of this study was to evaluate DAS's performance and capability in the treatment of contaminated mine water from an abandoned mine in Mpumalanga Province. Additionally, the study examined the effluent water's quality to determine whether it was suitable for domestic and agricultural use, as required by the regulations. By building on existing passive treatment performance literature, this thesis contributes to mine water treatment solutions in South Africa.

A pilot DAS system has been constructed to treat 2880 litres of acid mine drainage per day from an abandoned underground coal mine. The DAS is constructed using a combination of fine-grained alkaline material and coarse wood chips (e.g., limestone). The wood chips are porous, which aids in preventing clogging. Water quality was monitored, and preliminary results showed very high rates of contaminant removal (including SO_4 and Mn), which was attributed to the DAS systems' high rate of alkalinity additions. The pH in the DAS system increased to as high as 6.5 during the initial weeks of the experiments.

The system also neutralized the water and reduced pollutants such as Al, Cr, Zn, Ni, As, and Pb, but only a minor reduction in Fe was obtained (only a 15% removal rate was achieved). Following that, the quality of the treated water deteriorated over time due to blockage and/or depletion of the treatment components.

KEYWORDS AND PHRASES

Abandoned mines, Dispersed Alkaline Substrate, Passive treatment technologies**,** Polluted mine water

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LIST OF ABBREVIATIONS

ALD	Anoxic limestone drains
AMD	Acid mine drainage
CGS	Council for Geoscience
D&O	Derelict and ownerless mines
DAS	Dispersed alkaline substrate
DMR	Department of Mineral Resources
DWAF	Department of Water Affairs
EC	Electrical Conductivity
FA	Factor Analysis
GEMECS	Geology Exploration Mining Evaluation Consulting services
HDPE	High-density polyethene
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IUPAC	International Union of Pure and Applied Chemistry
LULC	Land use and land cover
MPRDA	Mineral and Petroleum Resources Development Act
NEMA	National Environmental Management Act
OLD	Open Limestone drains
PHE's	Potentially Harmful Elements
PRB	Permeable Reactive Barriers
SANS	South African National Standards
SAPS	Successive Alkalinity Producing Systems
SAWQG	South African water quality guidelines
TDS	Total dissolved Solids
WMA	Water Management area
WRC	Water Research Commission

1 INTRODUCTION

1.1 Background

Historic mines worldwide are notorious for their legacy of irreversible environmental impacts and health and safety hazards ranging from subsiding surfaces, mine fires, unsealed shafts, explosives, dust and Acid Mine Drainage (AMD) (Sibiya, 2019). These derelict mines are a common occurrence in South Africa where such mines operated before the promulgation of regulations such as the National Environmental Management Act (No. 107 of 1998) (NEMA) and the Mineral and Petroleum Resources Development Act, 2002 (MPRDA) (DMR, 2009). Derelict mines in the Witwatersrand Goldfield, Barberton Greenstone Belt, Pilgrim Rest Goldfield, Koegas Abestos field, Mafefe Asbestos Field and Witbank Coalfield bear testimony of the legacy of the historic mines (DMR, 2009).

The rehabilitation of derelict mines whose owners cannot be traced according to the Department of Mineral and Resources (DMR, 2009) criteria has put significant financial pressure on the South African government (Ogola, 2010). The Council for Geoscience (CGS) is currently conducting interdisciplinary research studies on behalf of the DMR to address environmental issues related to abandoned and ownerless mines in South Africa. The project's scope includes inventory surveys, which include identifying these abandoned mines, assessing the environmental and physical risks they pose, and possibly correcting any problems that are discovered.

The mandate of the Council for Geoscience includes:

- Identifying, locating and assessing all legacy mine hazards in South Africa.
- Ranking of all the mine hazards to prioritise rehabilitation to ensure public health and safety and to protect the physical environment.

This study is part of a larger national project that seeks to investigate the severity of mining impacts on the water resources and ecosystems of South Africa's river network, as well as to rehabilitate abandoned mines that pose a high risk to the environment.

Coal was mined in the Witbank coalfield as early as the 1900s as a source of energy and fuel for industries (Hobbs *et al.,* 2008). The rate of coal exploitation in the Witbank area increased dramatically in the 1970s, culminating in the construction of coal-fired power stations in 2008 (Adler and Rascher, 2007).

The coal mining industry experienced environmental challenges ranging from AMD, subsiding ground, pollution of streams and the exacerbation of potentially harmful elements (PHE's) and latter effects on the aquatic ecosystems (Adler *et al.,* 2007). These environmental woes are experienced during active mining operations and are worse in derelict mines where less maintenance and environmental stewardship is implemented (DMR, 2009).

Passive treatment is increasingly gaining favour compared to active treatment technologies because of its efficiency in removing contaminants at a reasonable cost, with regards to remediating polluted mine water. In the United Kingdom, several passive treatment technologies such as the Reducing and alkalinity producing system (RAPS) have been successfully implemented to manage polluted mine water from the derelict coal mines (Younger, 2000).

According to Skousen and Ziemkiewicz, (2005), hundreds of passive treatment systems have been built in the eastern United States over the last 20 years by reclamation programs, mining companies, and watershed organizations to provide reliable, financially feasible, low-maintenance mine water treatment technologies in remote areas. However, the application or implementation of these passive treatments has been limited and poorly understood in the South African context. The research study was an experimental assessment to investigate the success of dispersed alkaline systems in treating polluted mine water from the legacy coal mines.

This study adds to the existing literature on the resilience and capability of passive treatment while also contributing to mine water treatment solutions in South Africa. The aim of the study was to determine the capability of the DAS system in treating low volumes of mine impacted water to acceptable domestic water standards.

1.2 Project substantiation

According to Davenpoort (2006) and Balkau (1999), the South African government has a mammoth financial liability to rehabilitate derelict and ownerless mines, which operated in the past with no post-closure rehabilitation plan. The old Douglas Colliery in Mpumalanga Province is a typical existing example of a mine that neglected rehabilitation plans post closure. The uncontrolled discharge of polluted water emanating from the old mine works has altered the water quality, quantity and has caused severe environmental distress to the Klipspruit and Brugspruit (Hobbs *et al.,* 2008). Rivers are the main water source for domestic, industrial, and irrigation purposes, however, they are easily polluted because of their critical role in transporting mine impacted water and industrial pollution and runoff from agricultural land (Singh *et al.,* 2005). Poorly treated effluent has a detrimental impact on the aquatic ecosystem, agriculture, and the local community, and their economy. Monitoring effluent from treatment plants and the impact it has on the water quality of water resources is of utmost importance.

Polluted mine water is occasionally discharged from derelict mines into local streams, resulting in the acidification and regional salinization of surface waters (Van Niekerk *et al.,* 2001). This can be prevented by treating mine impacted water to a quality where it can be re-purposed for other uses. Van Zyl *et al.,* (2000) emphasized that for alternative re-use, the water needs to be neutral and adequately saturated with gypsum while for discharge into the sewer system the water needs to meet certain quality requirements as per the SANS 241:2015 standards and DWAF (1996) water guidelines. For irrigation, livestock watering or aquaculture, abnormal levels of potentially harmful metals need to be eliminated from mining effluent to make the water suitable for use.

The government of South Africa has become aware of the dangers posed by abandoned mining-related activities and has put in place efforts to deal with both past and active mining environments in South Africa. For instance, the Mine Closure and Rehabilitation Directorate in the Ministry of Mineral Resources have the task to oversee the rehabilitation of derelict mines where owners cannot be traced.

DMR is contributing towards mine water treatment solutions in South Africa by initiating projects aimed at conducting specialist research on derelict mines and proposing cost-effective, efficient and deployable water remediation technologies that can be used in treating polluted effluent water from derelict mines. Constructed wetlands have been proposed because of the advantages they have, such as low cost of maintenance, self-sustaining systems and the ability to treat a variety of contaminated wastewater as compared to other active treatment technologies. Uncertainty, however, still exists whether these systems can be used as long-term solutions for the removal of potentially toxic metals. Further research into sustainable passive water treatment of mine impacted water is required.

1.3 Study approach

The following approach was applied to complete the research:

- A Literature review of materials related to the subject of the research was reviewed to provide a background understanding. Also, research reports and papers, unpublished information and consultation with relevant stakeholders in the study area was done.

- Collection of hydrological data from local sources including the surrounding mines. Site visits, including an on-site sampling of the mine impact water, was done at chosen monitoring stations to determine the pH levels, Total dissolved solids (TDS), Electrical conductivity (EC) and concentrations of potentially harmful elements. However, the oxidation-reduction potential (ORP) measurements were not taken as a result of equipment malfunctioning. Monitoring of the water quality parameters was done before the pilot plant was constructed. The variables were chosen primarily due to concerns of high concentrations (above the permitted standards) being discharged into water resources, as well as potential impacts on downstream users/receptors.

- Influent and effluent sampling points were chosen. This allowed for a comparison of influent and effluent concentrations, which provided performance information. Samples were analysed for inorganic chemistry in the CGS laboratory for different parameters such as major and minor ions; the analytical methods performed included the inductively coupled plasma mass spectrometry (ICP-MS) and Ion chromatography.

- Results were compared against standards for drinking water and domestic use. The benchmarks from the South African National Standard for Drinking water (SANS

241:2015) and the South African water quality guidelines (DWAF 1996) were used for assessing the parameters from the samples.

1.4 Research aims and objectives

The study aims to evaluate the performance and capability of the Dispersed Alkaline Substrates (DAS) in treating polluted mine water from a derelict Colliery in Witbank, Mpumalanga Province of South Africa.

Specific objectives

- To undertake hydrogeochemical analyses of the input mine water (influent) and output (effluent) within the treatment system.
- To measure the performance and capability of the DAS system in reducing trace metals and sulphate.

The aim and objectives were selected to measure the performance of DAS system and determine whether there was a change in water quality after passing through the systems and whether water quality standards were being met. The research could contribute to a better understanding of DAS systems and their performance in the South African context. Although there are a number of operating Constructed Wetlands in South Africa there has been little performance data generally available to assist in the development of design and operational guidelines suitable to the South African water treatment characteristics, climate and treatment objectives. The majority of the installed systems appear to have been designed based upon reports on overseas systems, or simple rule-of-thumb assumptions.

Research questions

1. What are the physicochemical properties of the mine water, lime used in this research?
2. Can the DAS system reduce the potentially harmful elements to permissible discharge standards?
3. What is the effectiveness of the DAS system in treating polluted mine water?

1.5 Dissertation layout

The dissertation consists of five chapters outlined below:

Chapter 1: This section introduces the research topic, giving the background to the research, aims and objectives.

Chapter 2: This section discusses the different water treatment techniques. The chapter also discusses the concepts of constructed wetlands, their advantages and their limitations as compared to other passive treatment techniques. The chapter also highlights the laws regulating mining in South Africa, the significance of mining and the potential impacts generated from mining.

Chapter 3: This chapter details the materials and methods used for the construction of the pilot treatment, the operating principle of the system as well as how the sampling was conducted to obtain the data generated in the study. The chapter also describes the study area and the analytical methods used.

Chapter 4: Results and findings of the study are discussed in this chapter. Graphs and flow charts were used together to present these results.

Chapter 5: This chapter presents the main conclusions of the study and provides recommendations as to what other researchers can do to improve mine water treatment.

2 LITERATURE REVIEW

2.1 Mining in South Africa

South Africa has a lengthy history of mining and is rich in commodities such as gold, coal and platinum. The South African economy was founded on mining, after the discovery of diamonds in the Kimberley area in 1867. Since then, the sector has dominated the country's political economy and, while its direct contribution to gross domestic product is a relatively low 8%, the continuing influence of the mining sector on the political economy remains profound, even as the sector's paradigm has changed. The closure of mines typically results in often irreversible environmental degradation and economic hardship in mining-dependent communities, with the most severe impacts noted in the EMalahleni Coalfields and the Witwatersrand Goldfields.

A study conducted by Hobbs *et al.*, (2008) identified coal mining as the second biggest mining industry in South Africa after gold extraction. According to Munnik (2010) and Snyman (1998), coal is South Africa's most relied-upon source of energy, meeting approximately 70% of the country's necessities. Most of the coal produced and exported by South Africa is extracted from coalfields in the Mpumalanga Province.

However, coal mining is also one of the leading causes of water resource pollution both locally and globally (Mayes, 2005; Andy *et al.*, 1984). Tanner *et al.*, (1999) has described coal mining as the biggest contributor generating large volumes of mine wastewater in South Africa and has the potential to negatively affect the water resource if not properly managed. The problem has been exacerbated as a result of the neglect of environmental legislation in the past.

2.2 Mining legislature in South Africa

South Africa is a water-scarce country, and the quality of water determines its suitability for different uses (Conley, 1996; Turton *et al.*, 2006). According to Van Zyl (2002), water resource pollution is the most widespread environmental problem arising from the mining of coal. Factors such as the lack of policy before the promulgation of the Mineral and Petroleum Resources Development Act, 2002 (MPRDA) to address acid mine drainage at mine closure intensified the situation.

Mining operations historically had no regard for environmental protection, mining laws, or sustainable development, leaving open shafts, scattered waste spoils and tailings and vast areas barren and not productive, all of which have negative environmental and human health and safety consequences (Adler and Rascher, 2007; Hobbs *et al*., 2008). Consequently, AMD from abandoned coal mines created huge long-term environmental liabilities for the government (Adler *et al*., 2007). Mining, in general, pollutes water resources, pollutes the air and damages the natural landscape. Not only do local communities and ecosystems take direct strain but also worldwide, the mining industry contributes heavily to the human footprint.

The South African Minerals Act of (1991) was the first policy in South Africa to require all mining operations to practice sustainable land management rather than simply addressing aesthetic concerns. The MPRDA (2002) states in section 43 that:

"*The holder of a prospecting right, mining right, retention permit, mining permit, or previous holder of an old order right or previous owner of works that has ceased to exist, remains responsible for any environmental liability, pollution, ecological degradation, the pumping and treatment of extraneous water, compliance to the conditions of the environmental authorisation and the management and sustainable closure thereof until the Minister has issued a closure certificate in terms of this Act to the holder or owner concerned*".

The law empowers environmental authorities to investigate and control mining activities that may harm the environment. Since the implementation of the Minerals Act of 1991, the number of closure certificates in South Africa has declined to a point where very few are issued and this is evident from the number of abandoned mines and operations on extended care-and-maintenance, the on-selling of mines to less well-resourced companies to close, and the increase in illegal mining activities.

This act was repealed by the South African MPRDA of 2002 which states that "no closure certificate may be issued unless potential pollution to water resources is managed". Mine pre-planning must therefore include rehabilitation.

It is the government's strongest desire to rehabilitate all derelict and ownerless mines that endanger public safety and the environment to fulfil constitutional rights enshrined in Section

24 of the Republic of South Africa's Constitution, which assures everyone the following environmental rights:

a) “An environment that is not harmful to their health or well-being and
b) To have the environment protected for the benefit of present and future generations through reasonable legislative and other measures that;
    - Prevent pollution and ecological degradation;
    - Promote conservation; and
    - Secure ecologically sustainable development and use of natural resources while promoting justifiable economic and social development".

2.3 Environmental impacts of mining

Environmental and societal impacts associated with derelict and ownerless mines overwhelm governments globally (Sibiya, 2019). The degradation of the environment is an unavoidable consequence of mining activity. The range of environmental impacts from mining range from subsidence, emission of poisonous gases, explosives, acid mine drainage and stream divergence (UNEP, 2001). These environmental problems are well studied in the derelict and ownerless mines of South Africa, in Witbank Coalfields, Giyani Greenstone Belt, Barberton Greenstone Belt and Witwatersrand basin (Bell *et al.*, 2001; Ogola, 2010; McCarthy 2011; Mkhize, 2017; Tutu *et al.*, 2008). Various studies conducted in the Witwatersrand goldfields and the Witbank coalfields in South Africa revealed that pollution results from anthropogenic stressors including mining (Grobler *et al.,* 1994). Furthermore, abandoned mines discharging polluted water into the Olifants and Vaal Catchments have been reported to have adverse impacts on agricultural activities, threatening the coexistence between mining and agriculture (De Villiers and Mkwelo, 2009; Netshitungulwana, 2015; Sakala *et al*., 2017; Tutu, 2012).

Derelict mines in the Witbank Coalfield pose a huge financial calamity for the South African government and there is a need for urgent rehabilitation (Hobbs *et al.,* 2008). Environmental impacts are expected to persist long after mining operations have ceased, specifically those related to water quality and quantity. It is critical to ensure sustainable water treatment and/or management methods are investigated if not fully developed during the operational phase of a mine. This approach is believed to have the ability to reduce the water liability of the mine during closure.

The treatment of the mine effluent from the derelict coal mines presents a complex conundrum that requires a huge financial budget (Oelofse and Turton, 2008) occasioned by the geological locality and existing environmental conditions (UNEP, 2001). Treatment technologies have been developed globally to ameliorate discharge mine waters to acceptable chemical standards for drinking and industrial uses (Jenke and Pagenkpof, 1983; Rei and Schelmecka, 1990; Johnson and Hallberg, 2002; Domenech and Pablo, 2002; Erol *et al.*, 2005).

There were systems installed at Douglas Colliery mining area to manage the discharge from the old mine workings. These systems were classified into active treatment which employs chemicals and passive treatment which relies on natural and biological processes (Taylor, 2005). The use of passive treatment in South Africa has been limited and poorly understood (Novhe, 2012). The effluent treatment technologies generally aim at acid neutralisation and sulphate and metal removal (Taylor, 2005).

Many mines in South Africa are approaching the end lifespan and impacts on water quality will, therefore, persist if no alternative treatment methods are developed, especially for post-decommissioning sites. The use of biological passive treatment systems seems to be an attractive and economically sensible alternative to conventional technologies at abandoned mine sites for long term water treatment and relatively small contaminant loads. Theoretical explanations are available for the chemical and physical processes in passive treatment systems, and the basics seem to be well-understood, in principle. However, implementing biological water treatment systems is still regarded as "tricky" by practitioners, the public and, perhaps most important, regulators (McCarthy and Pretorius, 2009).

2.3.1 AMD formation

The formation of AMD occurs when water flows on the geological strata with exposed sulphate bearing materials mainly pyrite, exposed to oxidising environmental conditions. Council for Scientific and Industrial Research (CSIR, 2009) and Makgae (2012) reported that the processes are complicated as the geochemistry, temperature, micro-organisms and physical characteristics vary greatly in different environmental settings.

The most common mineral involved in acid mine drainage is pyrite (FeS_2). When pyrite is exposed to atmospheric oxygen and water, it gets oxidized, resulting in the release of hydrogen ions, acidity, sulphate ions, and soluble metal cations, as shown in $2FeS_2$ (s) + $7O_2$ (aq) + $2H_2O$ → $2Fe^{2+}$ + $4SO_4{}^{-2}$ + $4H^+$………………………………………. (Equation 1). This oxidation process occurs at a slow pace and allows the water to buffer the acid generated in the rocks.

$2FeS_2$ (s) + $7O_2$ (aq) + $2H_2O$ → $2Fe^{2+}$ + $4SO_4{}^{-2}$ + $4H^+$………………………………………. (Equation 1)

Fe^{2+} (ferrous iron) is further oxidized to Fe^{3+} (ferric iron) consuming one mole of hydrogen ions per mole of ferrous iron $2Fe^{2+}$ + ½ O_2 + $2H^+$ → $2Fe^{3+}$ + H_2O ……………………………………………………………….. (Equation 2).

$2Fe^{2+}$ + ½ O_2 + $2H^+$ → $2Fe^{3+}$ + H_2O ……………………………………………………………….. (Equation 2)

Fe^{3+} in this stage further releases hydrogen ions. Ferric iron can either precipitate as iron hydroxide (ochre) (Fe $(OH)_3$ the red-orange precipitate (ferric hydroxide or yellow boy) (see **Figure 1**) seen in waters affected by acid mine drainage or it can react directly with pyrite to produce more ferrous iron and acidity as shown in reactions $2Fe^{3+}$ + $6H_2O$ → 2Fe $(OH)_3$ (s) + $6H^+$ ………………………………………………… (Equation 3) and $14Fe^{3+}$ + FeS_2 (s) + $8H_2O$ → $2SO_4{}^{-2}$ + $15Fe^{2+}$ + $16H^+$ ……………………………….. (Equation 4).

Figure 1: Red to orange precipitate seen in waters affected by acid mine drainage (DWA, 2010)

$2Fe^{3+} + 6H_2O \rightarrow 2Fe(OH)_3(s) + 6H^+$ ………………………………………………… (Equation 3)

$14Fe^{3+} + FeS_2(s) + 8H_2O \rightarrow 2SO_4^{-2} + 15Fe^{2+} + 16H^+$ ……………………………….. (Equation 4)

When Fe^{2+} is produced as a result of $14Fe^{3+} + FeS_2$ (s) + $8H_2O \rightarrow 2SO_4^{-2} + 15Fe^{2+} + 16H^+$ ……………………………….. (Equation 4) and there is sufficient dissolved oxygen the cycle of equations 2 and 3 is propagated (Younger, *et al*., 2002).

In the absence of dissolved oxygen, (Equation 4) will be completed, and water will contain high levels of ferrous iron (Younger, *et al.*, 2002). Lekoadu (2015) reported that these reactions occur at a very slow rate under low pH. He continues by stating that microorganisms play a critical role in accelerating the chemical reactions that occur during the formation of mine drainage. The bacteria Acidothiobacillus are frequently mentioned in various literature.

These bacteria catalyse the oxidation of ferrous iron, further prolonging $2Fe^{2+} + ½ O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O$ ……………………………………………………………….. (Equation 2 and through 4). Though not a significant source of acidity, the formation of hydrogen ions when certain metals precipitate must be considered when determining treatment options.

$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$ ……………………………………………………………………….(Equation 5)

$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$ (see equation 3) ……………………………………………….(Equation 6)

$Fe^{2+} + 0.25\ O_2(aq) + 2.5\ H_2O \rightarrow Fe(OH)_3 + 2H^+$ ……………………………………………..(Equation 7)

$Mn^{2+} + 0.25\ O_2(aq) + 2.5\ H_2O \rightarrow Mn(OH)_3 + 2H^+$ …………………………………………….(Equation 8)

According to Younger *et al.,* (2002), several additional metal sulfides may release metal ions into water but do not produce acidity; the reason for this is unknown. Some of the metal sulphates includes:

Sphalerite $ZnS(s) + 2O_2\,(aq) \rightarrow Zn^{+2} + SO_4{}^{-2}$ ………………………………………………… (Equation 9)

Galena $PbS(s) + 2O_2\,(aq) \rightarrow Pb^{+2} + SO_4{}^{-2}$……………………………………………………… (Equation 10)

Millerite $NiS(s) + 2O_2\,(aq) \rightarrow Ni^{+2} + SO_4{}^{-2}$ ………………………………………………….. (Equation 11)

Greenockite $CdS(s) + 2O_2\,(aq) \rightarrow Cd^{+2} + SO_4{}^{-2}$ ……………………………………………… (Equation 12)

Covellite $CuS(s) + 2O_2\,(aq) \rightarrow Cu^{+2} + SO_4{}^{-2}$ …………………………………………………… (Equation 13)

Chalcopyrite $CuFeS_2(s) + 4O_2\,(aq) \rightarrow Cu^{+2} + Fe^{+2} + SO_4{}^{-2}$ ……………………………………. (Equation 14)

2.3.2 Economic and Environmental impacts of AMD

Acid mine drainage has a significant negative impact on the profitability of a mine operation. Several factors could contribute to this, including the damaging effects on infrastructure and equipment of acid water (Dlamini, 2010), limitations on water reuse and discharge, and the high cost of implementing effective closure plans.

AMD releases potentially harmful metals into the surrounding environment. As a result, metals enter the food chain via the aquatic system. AMD can have severe consequences for stream ecology, affecting the beneficial use of watercourses downstream of mining operations. Jennings *et al.,* (2008) say that fishes are exposed to metals directly through their gills in water, which leads to the impairing of respiration as a result of chronic and acute toxicity.

Chemical reactions occur quickly in mined-out areas due to the easy access of air through mine works, wastes, and tailings, as well as the larger surface areas of sulphides in these. According to Akcil and Koldas, (2006) AMD, is widely regarded as one of the most serious environmental hazards associated with mining sulphide ore deposits. This is primarily due to a decrease in the pH of nearby water and soils and/or an increase in heavy metal concentrations.

AMD has become a highly evident and politically charged issue in South Africa (Akcil and Koldas, 2006) as it threatens the water resources, human health and food security in mining areas. Mine closures, combined with the increase of acid mine drainage, have a negative impact on communities that were previously reliant on the mining industry (Akcil and Koldas, 2006).

South Africa’s prosperity relies highly on mining for the creation of jobs and economic prosperity. Mining plays an integral part in a community’s well-being. However, one must understand that mining has an impact and that water will always be inseparably linked to the mining process.

The impacts of AMD can be summarized as follows:

- Mobilises potentially harmful metals (such as aluminium, manganese) to levels unfavourable to aquatic ecosystems
- Renders ecosystems uninhabitable
- Changes in water chemistry disrupt important life-supporting balances, resulting in the formation of chemical precipitates that can suffocate aquatic habitats and reduce light penetration.

2.4 Potentially harmful metals

Passow *et al.* (1961) define potentially hazardous metals as “individual metals and metal compounds that negatively affect people's health and animals at high concentrations” (Antonovics *et al.,* 1971). These metals occur naturally in rocks and are released to the environment through the process of weathering. Humans rely on aquatic environments for a variety of ecosystem services, but they frequently receive high levels of pollution from both point and non–point sources (Anon, 1993; Anon, 1997). According to Gagnon *et al.* metal availability in polluted wastewater is influenced by the physical and chemical conditions of the wastewater and the receptor (2006). Most metals are removed from effluents and end up in the solids produced during wastewater treatment. Iron, aluminium, and manganese are the most frequently occurring metals in AMD.

2.5 Treatment of mine water

The most appropriate treatment technology is determined by the quality and quantity of mine water, as well as the derived quality of resultant treated water.

Nkongolo *et al.* (2019), explain that the goal of treating AMD is to add alkalinity into the water to neutralize the acidity, remove potentially harmful elements through precipitation or adsorption and reduce sulphate concentrations in mine water.

Traditional active water treatment technologies, such as chemical treatment, can be effective in meeting water quality goals. These systems, however, are associated with high construction and maintenance costs (Johnson and Hallberg, 2005).

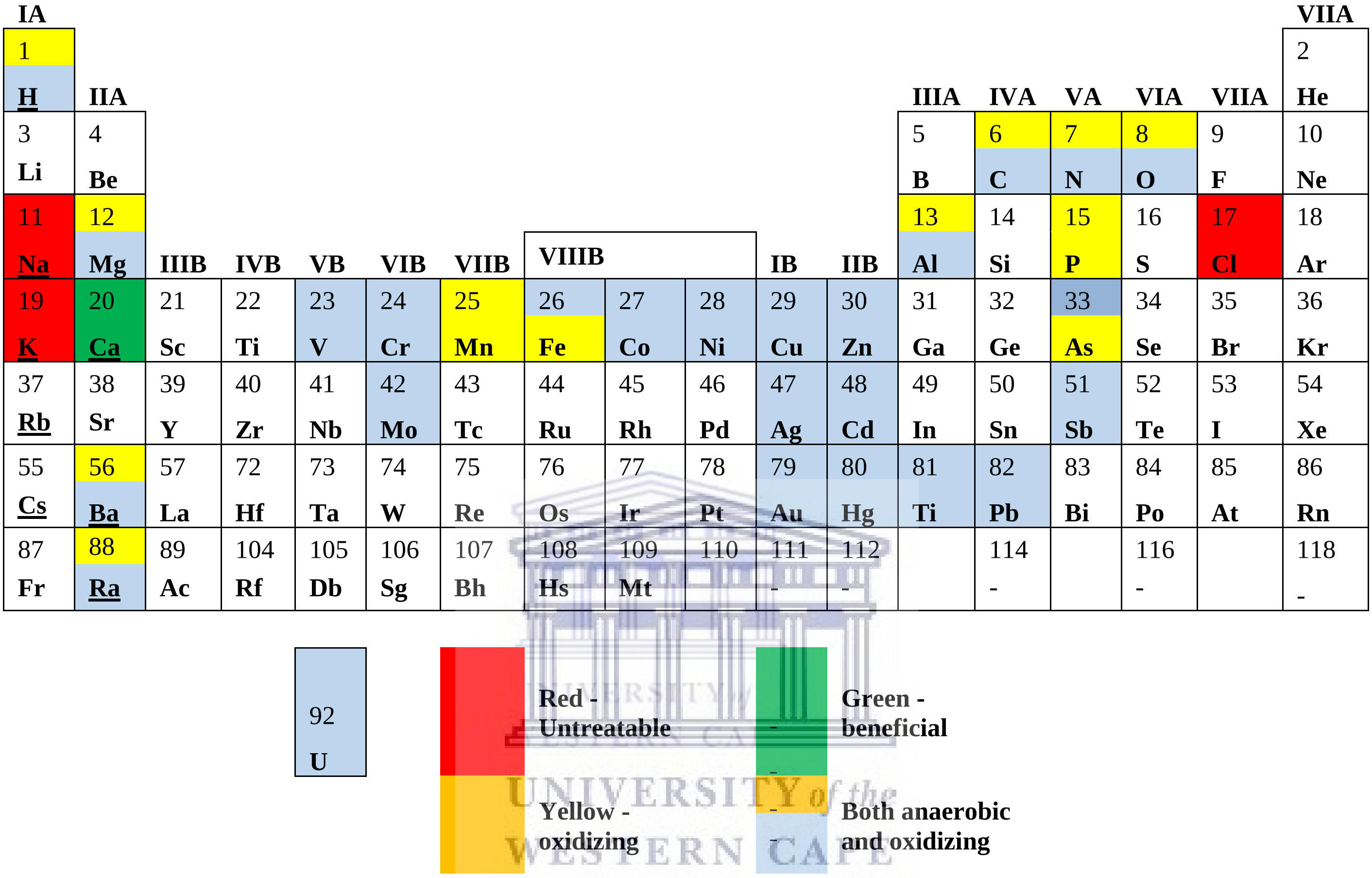
The development of effective passive techniques to supplement active technologies has the potential to reduce the water management liability associated with mining activities, particularly for sites where mining has ceased. Studies by (Younger, 2001, Wamsley and Mazury, 1999) have focused on the impact acid mine drainage has on the receiving environment. Some case studies indicate that water originating from mine residue deposits might have near-neutral pH conditions (Johnson and Hallberg 2005), but still have a detrimental impact due to elevated sulphate concentrations (Madzivire *et al.,* 2009).

2.5.1 Evaluation of passive treatment applicability

The Gusek (2009) periodic table for passive treatment was used to assess the suitability of a passive treatment system based on water chemistry and flow rate. (Figure 2). The periodic table of passive treatment is based on the principle of redox chemistry. Chemical constituents highlighted in blue (such as Cr, Zn, Ni, V) can only be treated under reducing conditions, whereas those highlighted in orange can only be treated under oxidizing conditions. However, some of the chemical constituents are highlighted in both blue and orange colours (such as Fe, Al, As, Ba), meaning that they can be treated under both conditions. Those highlighted in red (Cl, Na, K) are untreatable. This periodic table is important when it comes to the sequencing of different passive treatment systems such as:

- Anaerobic Sulphate-reducing Bacteria (SRB) bioreactors.
- Dispersed Alkalinity Substrate (DAS) (Rötting *et al.,* 2008).

Such systems include everything from proven technologies that work at full scale to promising technologies that have yet to be demonstrated at full scale to emerging technologies that have only been studied in the laboratory.



IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIA
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111 -	112 -		114 -		116 -		118 -

92
U

🟥 Red - Untreatable

🟩 Green - beneficial

🟨 Yellow - oxidizing

🟦 Both anaerobic and oxidizing

Figure 2: Periodic table for Passive Treatment (adapted from Gusek 2009)

2.5.2 Active treatment technologies

A study done by Madzivire *et al.*, (2012) contends that active treatment systems are defined as "systems that improve the quality of water by processes that requires regular operation and maintenance, uninterrupted input of artificial power and dosing of biochemical or chemical reagents". The addition of an alkaline substance, primarily calcium carbonate, to mine effluent during active treatment raises the pH (Novhe, 2012). This is effective in the oxidation of ferrous iron and precipitation of some potential harmful elements (Sangita, 1988). The primary advantage of active treatment systems is their ability to adapt to changes in mine water quality and quantity. This is a result of the precision with which processes are controlled in response to these changes. These neutralising agents include;

- Hydrated lime ($Ca(OH)_2$)
- Quicklime (CaO)
- Caustic soda ($NaOH$)
- Soda ash (Na_2CO_3)
- Ammonia (NH_3)
- Magnesium oxide / hydroxide (MgO / $Mg(OH)_2$)
- Mineral carbonates

Chemical precipitation, reverse osmosis, crystallisation, and biological sulphate reduction are just a few of the active treatment technologies available (Eary *et al.*, 1990; Erol *et al.*, 2005).

2.5.2.1 Chemical precipitation

Chemical precipitation involves the precipitation of potentially harmful elements under specific pH that form insoluble precipitates using alkaline materials (Stenzel and Gunther, 2005). These alkaline materials aid in increasing the pH of the AMD while accelerating the chemical oxidation of Fe^{2+}, to precipitate as hydroxides. A simplified schematic representation of a chemical precipitation process during water treatment is shown below in Figure 3.

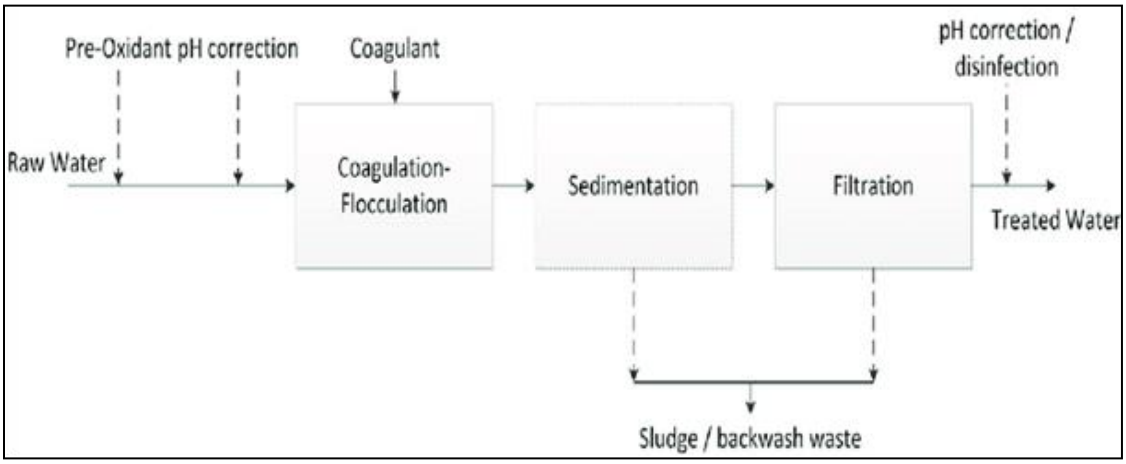


Figure 3: The schematic representation of a chemical precipitation process for water treatment (adapted from Pohl, 2020).

2.5.2.2 Reverse Osmosis (Membrane technology)

This process involves the passing of acid water through a semi-permeable membrane (Pulles *et al.*, 2001). Reverse Osmosis (RO) removes most dissolved solids from polluted mine water and treats water to high quality. The RO method relies on limestone and/or lime dosing as well as aeration to neutralize acidic water and remove dissolve potentially harmful metals. Before RO, filtration is performed using either sand and cartridge filters or ultrafiltration. The acid water is forced through the membrane, allowing only the solvent to pass through (Pulles *et al.*, 2001). A single-stage RO plant can achieve a recovery rate of 50-80%, and multiple stages can increase this to 95% see Figure 4.

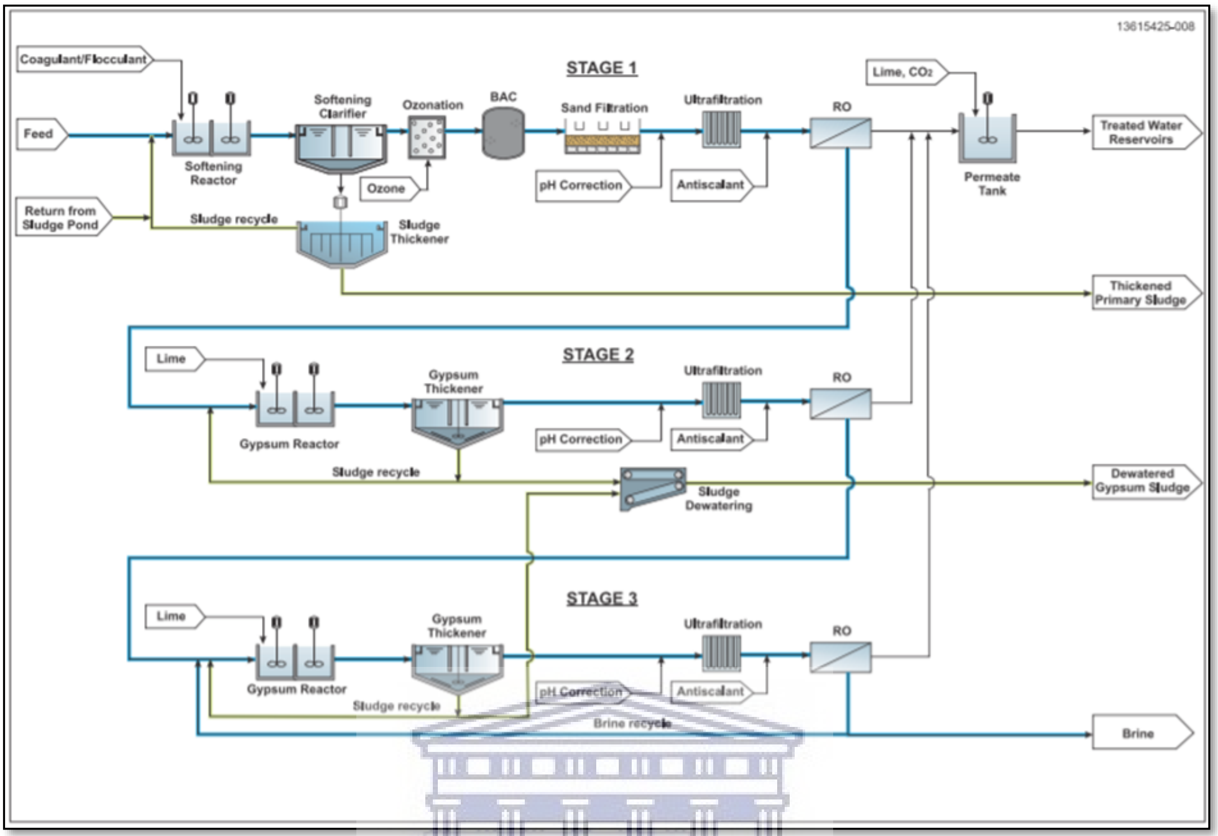


Figure 4: Example of a reverse osmosis membrane treatment (adapted from Samaei *et al.*, 2020)

2.5.2.3 Crystallisation

The crystallisation treatment process aims at decreasing the sulphate concentrations in the mine water (Johnson, 2000). Crystallization of sulphates is achieved through the pre-treatment of the mine water to adjust the pH thus decreasing the metal concentrations (Motsi, 2010). The principle of the process is as follows: when a solution containing dissolved contaminants is slowly frozen, ice crystals form and rise to the surface, while contaminants become concentrated in the remaining solution and eventually crystalize out at the eutectic temperature (see Figure 5). The crystals can be separated from the major liquor, washed and melted to yield nearly pure water (Lewis *et al.*, 2010)

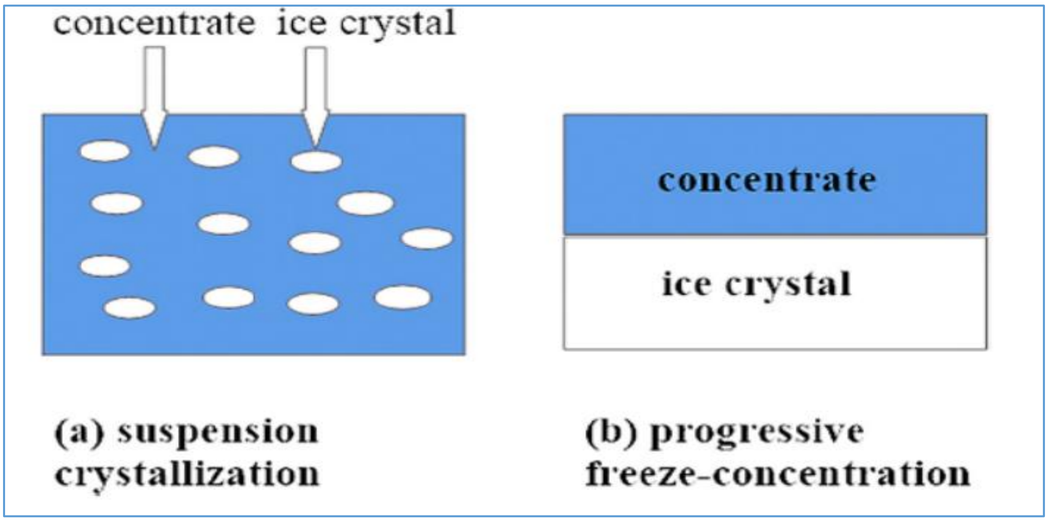


Figure 5: Schematic diagram of suspension freeze crystallization (a) and progressive freeze concentration (b) (Lu et al., 2017).

2.5.2.4 Chemical biological sulphate reduction

Biological sulphate reduction uses organic substrates and additional chemicals to reduce the concentration of sulphate in the mine water (Zagury *et al.*, 2007). Sulphates act as a reducing agent in the biological sulphate reduction process, while the organic substrate acts as an oxidizing agent (Zagury *et al.*, 2007). The configuration of a standard biological sulphate removal procedure is shown in Figure 6 below.

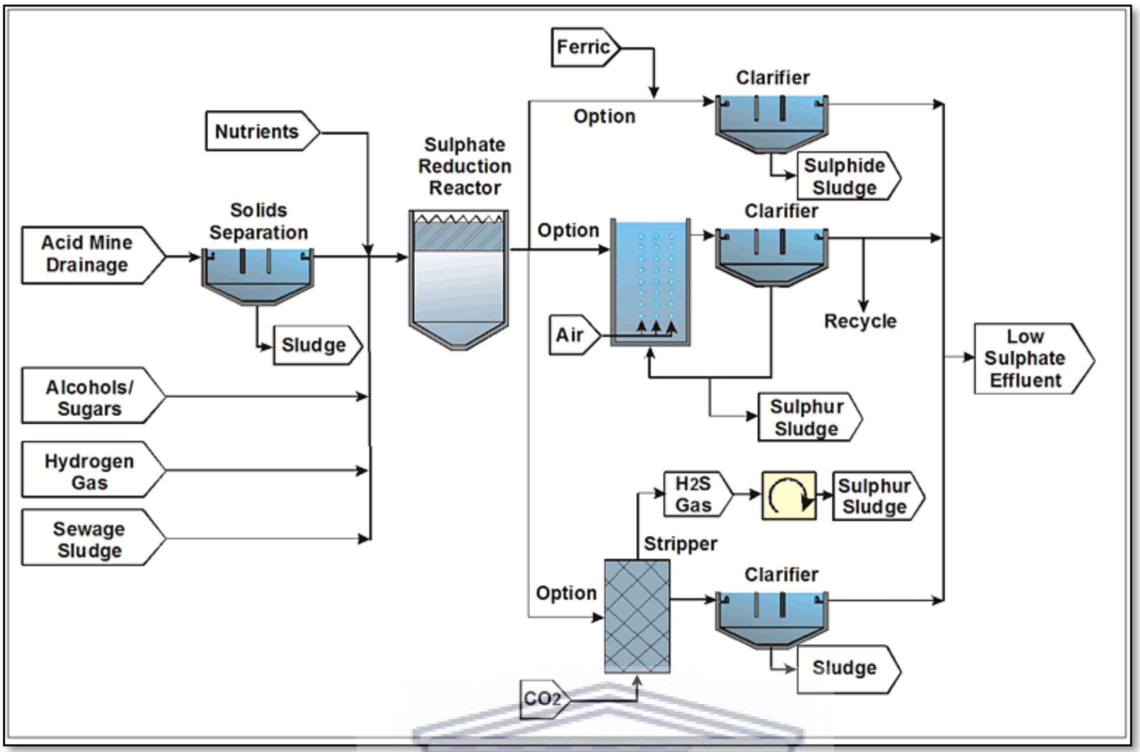


Figure 6: Configuration of the biological sulphate removal technique (adapted from GARD Guide 2009).

2.5.3 Passive treatment technologies

The Environmental Protection Agency (EPA 2000) describes passive treatment technologies as self-operating systems without human interference to treat mine water over a specified period to considerable discharge standards. Passive treatment technologies are considered to be self-operated based on filtering mine water pollutants without taking a strain on a prescribed period (USGS, 2001). These innovative technologies utilise physical, geochemical and biological mechanisms to treat impacted mine water (EPA, 2000).

Eres *et al.* (2005) iterated that passive treatment systems are globally favoured for mine water treatment technology because of their ability to neutralise mine water with no additional inputs over longer periods. There is a wealth of documentation on various passive treatment techniques and design criteria specific to mine-water treatment (McCauley, 2011). On the other hand, in South Africa, there is limited information or application of passive treatment systems at a large scale since most of the research was a laboratory scale (Novhe *et al.*, 2016).

According to Pulles *et al.*, (2001), the effectiveness of passive treatment systems is dependent on the retention time and volume of mine water required to be neutralised, as well as the chemical complexity of the mine water. Because of their ability to promote the activity of sulphate reducing bacteria that generate alkalinity, raising the pH, and thus precipitating potentially harmful elements and sulphates, the effectiveness of these systems has been very variable (Kilborn, 1999; Eres *et al.*, 2005). Furthermore, the passive treatment systems offer a valuable option for treating mine water at remote locations. Passive treatment systems are effective in addressing post-closure mine water (Klink 2004). The major processes employed in the passive treatment system include:

- Chemical
  - Oxidation/reduction
  - Coagulation
  - Adsorption/absorption
  - Hydrolysis and precipitation
- Physical
  - Gravity
  - Aeration, and
  - Dilution
- Biological
  - Biosorption, bioreduction
  - Biomineralization, and
  - Alkalinity generation.

Passive treatment technologies are dependent on factors that include the geology thus, the geochemistry of the mine water to be treated and existing climatic conditions of the area (Zipper *et al.*, 2011). Several passive treatment technologies (e.g. Reducing and alkalinity producing systems) have been documented worldwide aimed at addressing issues associated with mine water pollution.

2.5.3.1 Constructed Wetlands (CWs)

Constructed wetlands (CWs) are defined as “complex, interconnected systems of water, plants, animals, microorganisms, and the environment” (Younger *et al.,* 2002,). A study conducted by Robb and Tobinson (1995), reported that these systems utilise soil, organic material, rocks, and wetland plants as a substrate to host and facilitate microbial processes for water treatment. Depending on the contaminant removal mechanisms required, these systems can be aerobic or anaerobic (Costello, 2003). While wetlands are self-adjusting systems in general, understanding how natural wetlands are structured and function greatly increase the likelihood of successfully constructing a treatment wetland.

CWs are introduced globally to treat wastewater because of their ability to save money and energy. The use of CWs however has several limitations, which include treatment performance variability and unpredictability.

Research has been conducted on the use of CWs in reducing potentially toxic elements from mine impacted water. Uncertainty, however, still exists whether these systems can be used as a long-term solution for effective and sustainable removal. The gaps specifically relate to the performance and flow conditions that can be expected under field conditions, as well as the suitability of substrates to host sulphate-reducing bacteria to reduce potentially toxic elements in mine impacted water. There have been limited studies in South Africa dealing with the application and performance of CWs in treating mine impacted water.

2.5.3.2 Anaerobic and Aerobic Wetlands

Anaerobic retention ponds operate in an oxygen suppressed environment and are comprised of organic material and limestone aggregate substrate (see Figure 7). Sulphate-reducing bacteria must be present in the organic material for metal sulphide precipitates to form (Robb and Robinson (1995). Anaerobic wetlands are the most widely used passive treatment systems for AMD, and before dissolved metals can precipitate, the wetland must reach pH levels above 7.

The following two mechanisms are used to treat anaerobic ponds based on alkalinity addition: sulphate reduction, which converts $SO_4{}^{2-}$ into H_2S in an organic-rich environment lacking oxygen, releases alkalinity as follows:

$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3$……………………………………………………… (Equation 15)

As shown in CaCO3 + **H+ → Ca2+ + HCO3-**……………………………………………………………… **(Equation 16**), H^+ ions drive the dissolution of $CaCO_3$, producing calcium ions and bicarbonate ions. The bicarbonate ions formed then react with the remaining hydrogen ions, consuming more acidity.

$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3$-……………………………………………………………… (Equation 16)

Aerobic wetlands are shallow open ponds promoting the oxidation and precipitation of potentially harmful elements (Nairn *et al.*, 1992). These wetlands are intended to aid metal precipitation during the oxidation process. Aerobic systems are mostly used for metal precipitation from AMD (Skousen and Ziemkiewicz, 2005).

The quantities of dissolved metals, DO concentrations, pH of the mine water, active microbial biomass, and the residence time of the water in the wetland all have a role in the efficacy of metal removal in these systems.

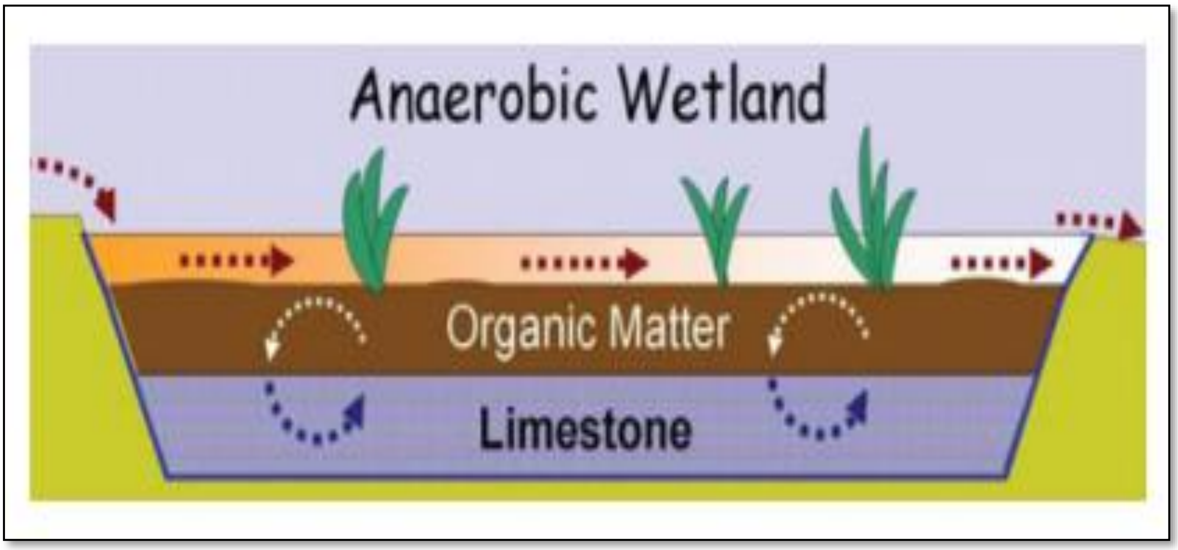


Figure 7: Simplified design criteria used for constructing aerobic and anaerobic wetlands (adapted from Zipper *et al.*, 2014)

2.5.3.3 Anoxic limestone drains (ALD)

Passive treatment systems, according to Younger (2000), allow mine water to flow through rich carbonate oxide substrates via gravity. The system employs a permeable underground limestone bed through which the untreated mine water passes where the acid-rich mine water dissolves the carbonate oxide rich substrates to generate alkalinity to the effluent increasing the pH, thus precipitation occurs.

Figure 8: The setup of an Anoxic Limestone Drain system (Zipper *et al.*, 2018).

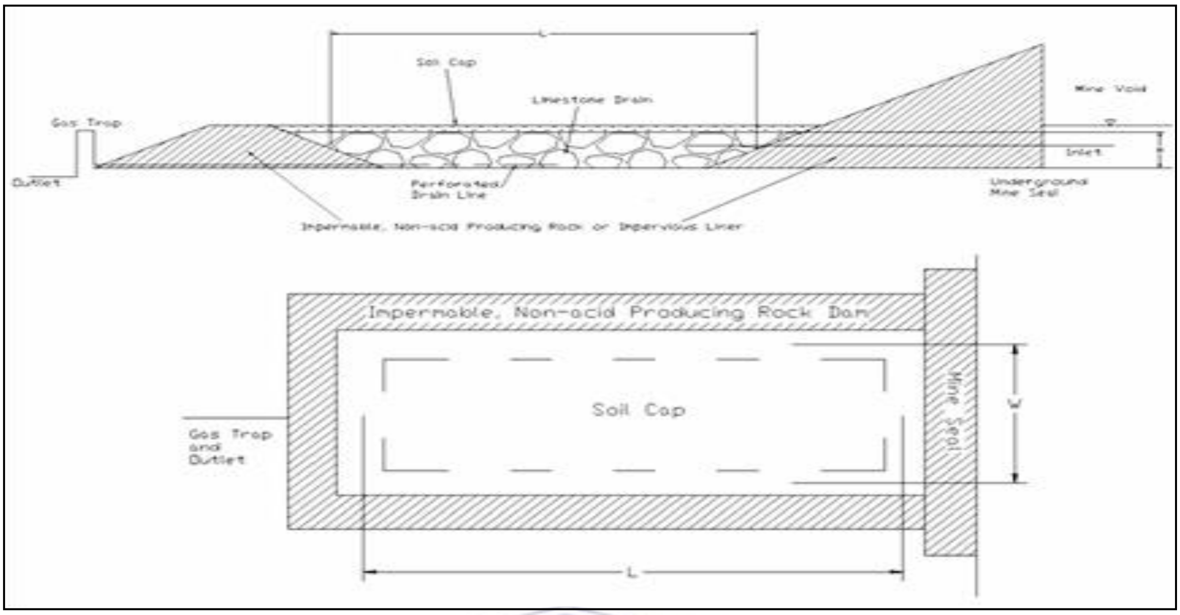


Figure 8 and

Figure 9 show a typical setup of an ALD system where the influent anoxic water is treated with limestone in a closed system and subsequently released to a settling pond through a standpipe.

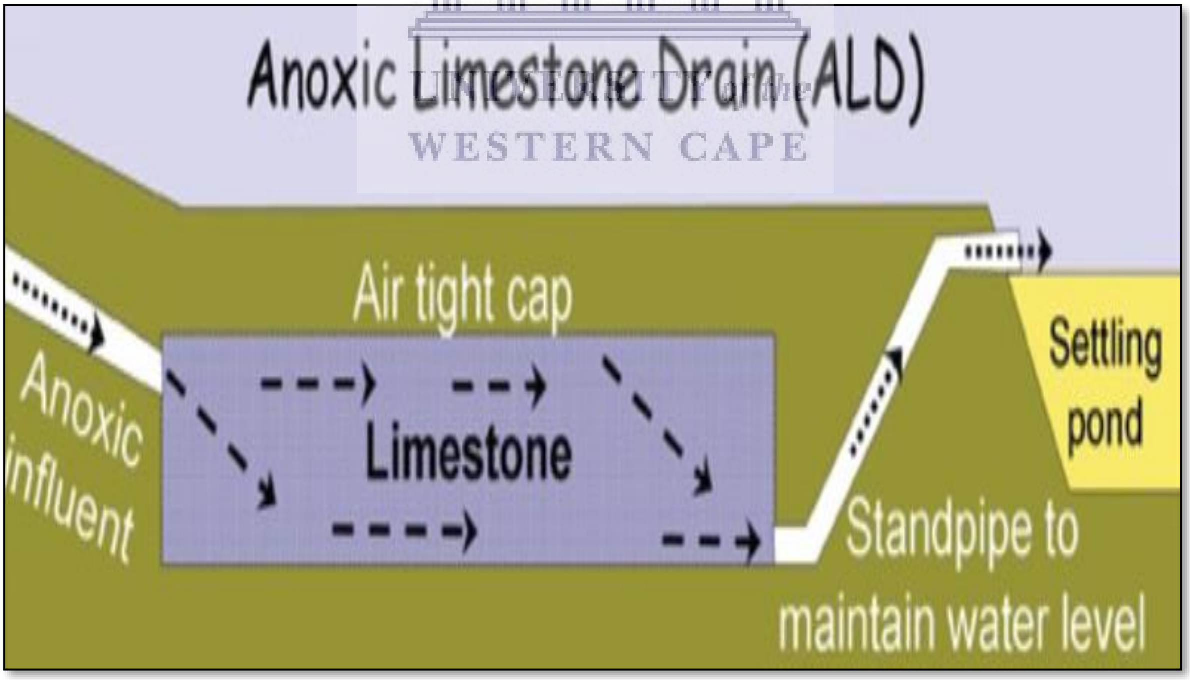


Figure 8: The setup of an Anoxic Limestone Drain system (Zipper *et al.*, 2018).

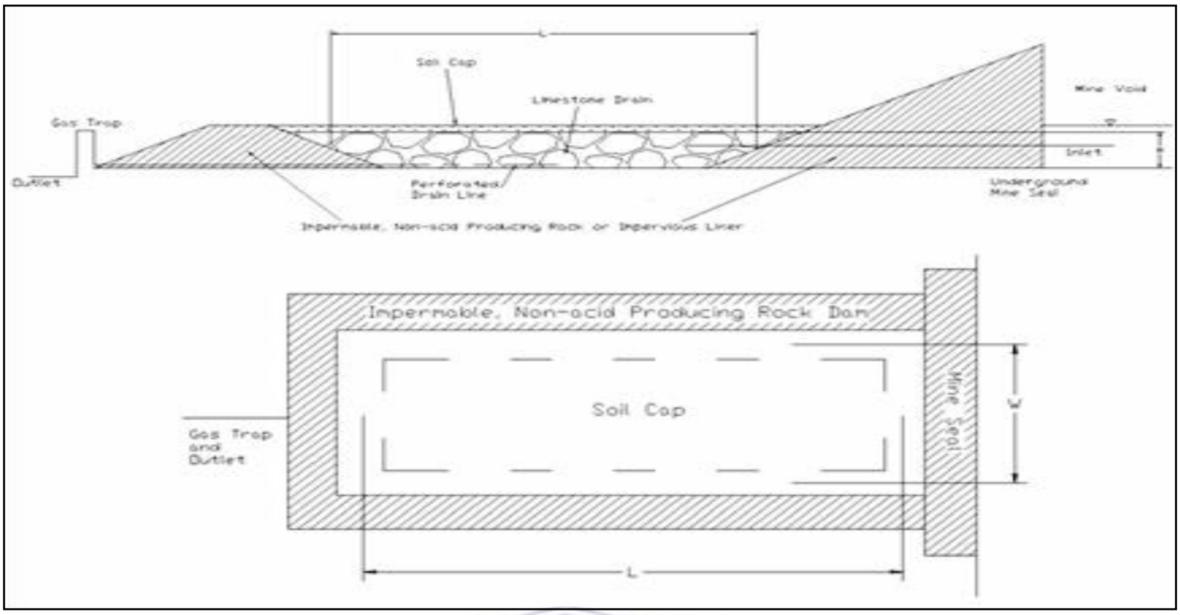


Figure 9: Anoxic Limestone Drains general design (Skousen and Faulkner, 1992).

2.5.3.4 Successive alkalinity producing systems (SAPS)

Mine water is passed through a carbonate oxide rich substrate before being subjected to an organic matter rich substrate during treatment (Ziemkiewicz *et al.*, 2003). Costello (2003) explains that acid-rich mine effluent is buffered when passing through carbonate-rich limestone due to dissolution of carbonates thus elevating the pH and further undergoing Sulphate Reducing Bacterial (SRB) activity through the organic-rich substrate (See Figure 10). According to Skousen *et al.*, (2017b) insisted that the organic layer mainly reduces total iron (Fe) to ferrous iron (Fe) and minimizes the coating of limestone with ferric hydroxide. Furthermore, the organic layer contributes to acid neutralization through sulfate reduction. Perforated pipes are buried into the limestone to allow water to flow into an aerobic wetland, where iron (Fe) and manganese will precipitate (Mn).

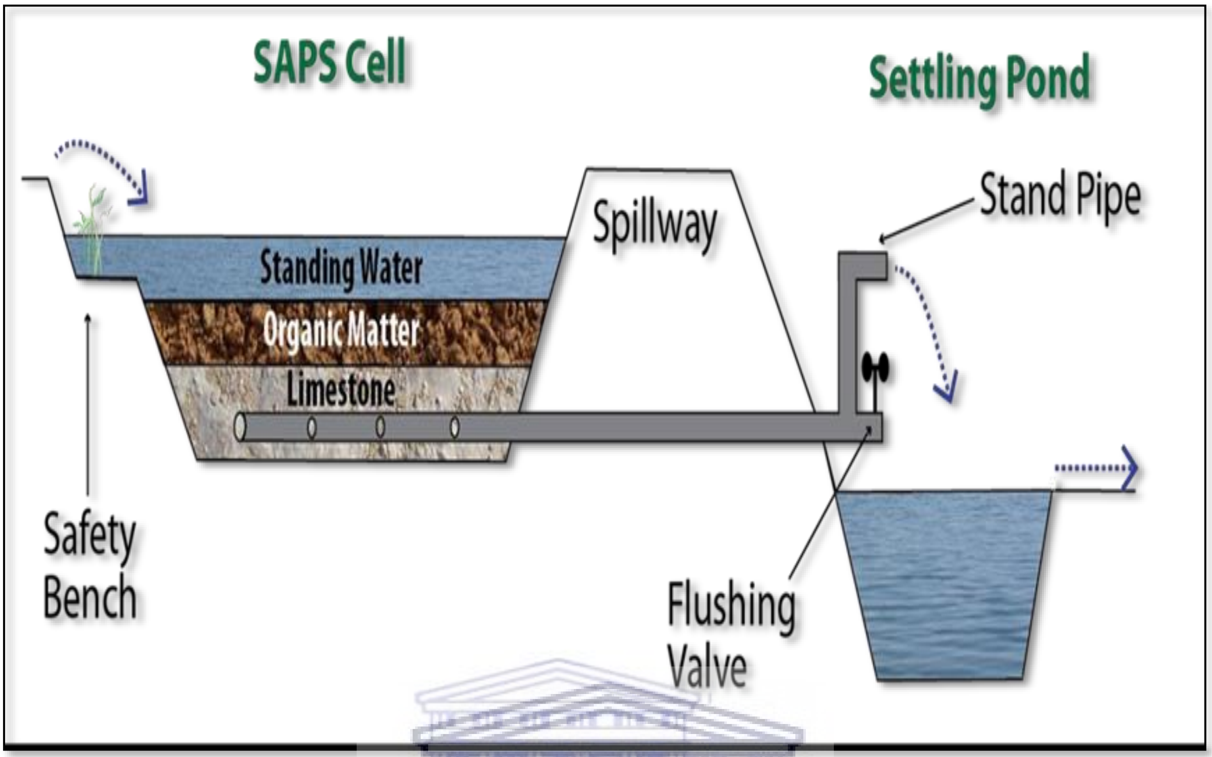


Figure 10: Setup of a vertical flow wetland (SAPS) (Zipper and Skousen, 2014).

2.5.3.5 Permeable reactive barriers (PRB)

Permeable Reactive Barriers (PRB) employ permeable barriers of carbonate oxide underground as a treatment substrate for underground water plumes (Faisal *et al.*, 2018). PRBs typically involve the emplacement of layers of reactive material such as limestone and organic matter in the subsurface across the contaminated groundwater flow path (Taylor *et al.*, 2005b; Thiruvenkatachari *et al.*, 2008) as shown in Figure 11 below. These systems are ideal for the *in-situ* treatment of groundwater affected by AMD (Ramontja *et al.*, 2010). Through microbial processes, the organic matter/compost in the system supports sulfate reduction, creating alkalinity and increasing metal precipitation in the permeable barrier (Johnson and Hallberg, 2005a).

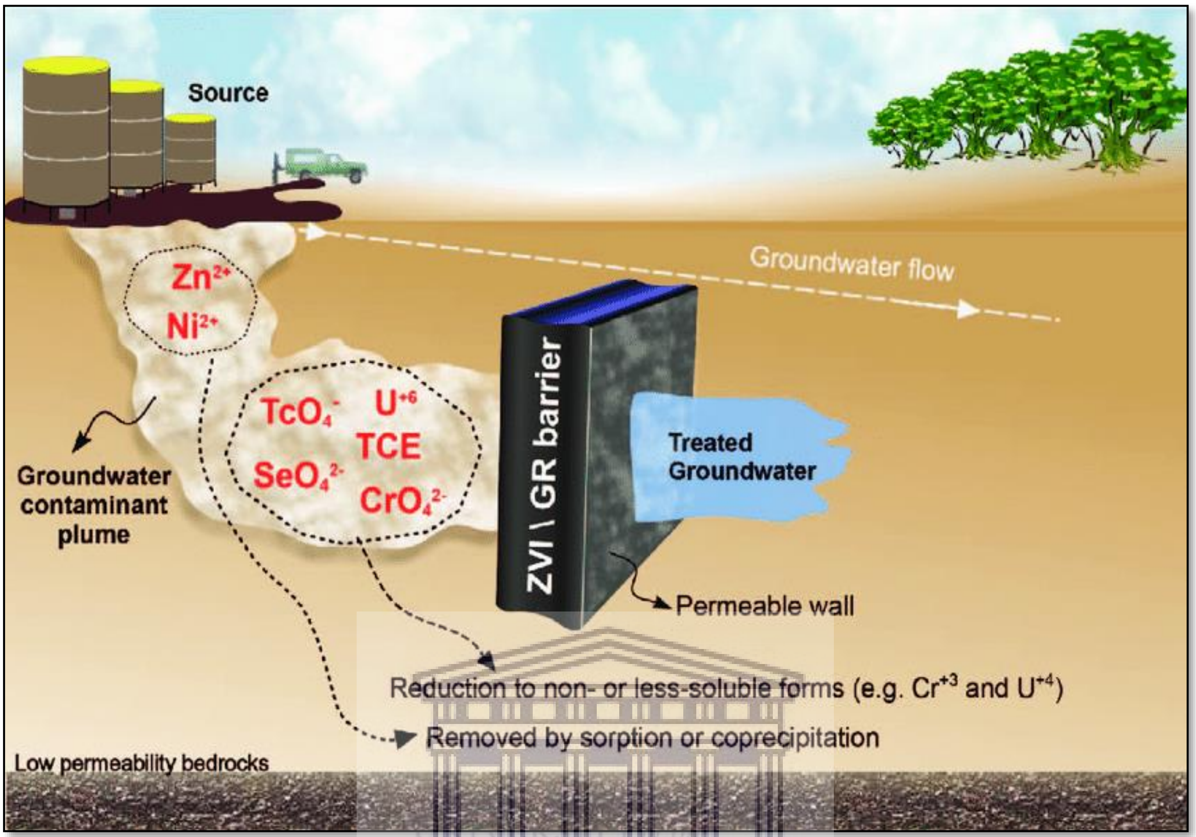


Figure 11: Typical PRB used for containing groundwater plumes (Ahmed *et al.*, 2010).

2.5.3.6 Phytoremediation

Lekoadu (2015) describes phytoremediation as an “emerging approach that uses various plants to eliminate, transfer, maintain, extract or degrade pollutants from soil and water” (see Figure 12). The method thus relies on green plants, fungi, algae, bacteria and microbial mats for the removal of potentially harmful metals (Lekoadu, 2015). Various authors such (Fasani *et al.*, 2018) also reported that polluted sites can be remediated by naturally occurring plants. The plants take up the toxic metals because they require minerals and vitamins for nourishment and to achieve their full life cycles.

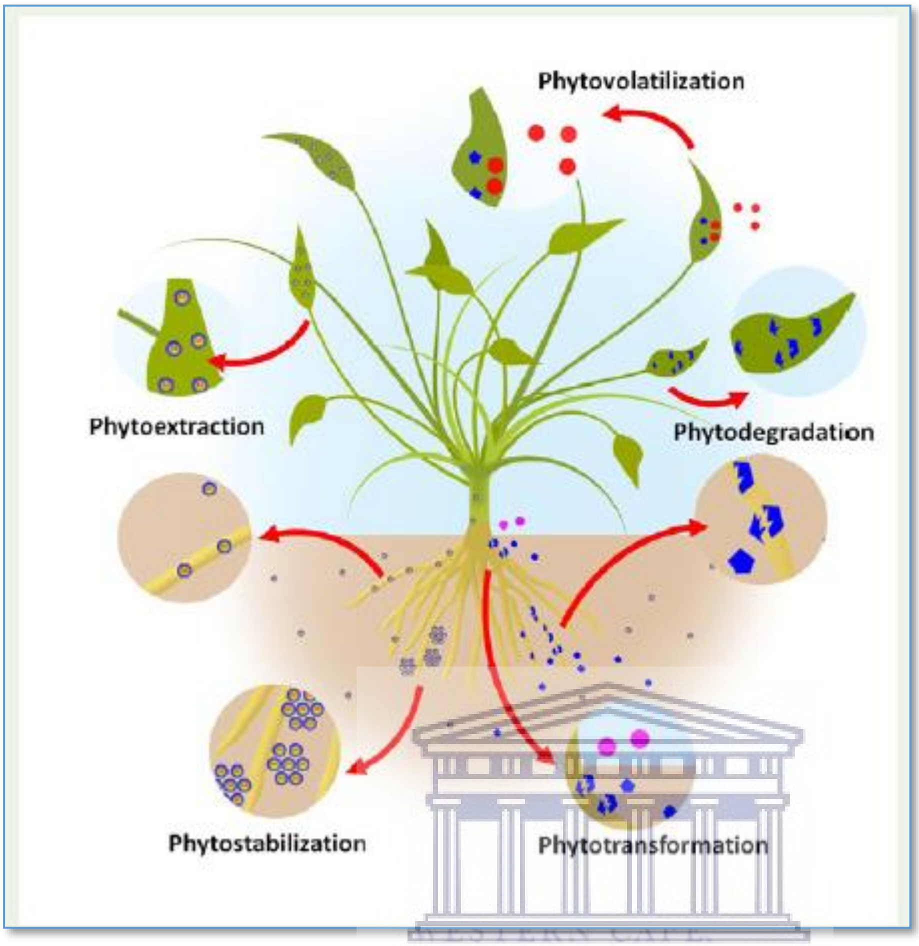


Figure 12: Schematic representation of the phytoremediation technique (Source: http://opensciencepublications.com/)

2.5.3.7 Advantages and Disadvantages of Active, and Passive treatment technologies

Table 1 summarizes the advantages and disadvantages of active and passive treatment technologies.

Table 1: Advantages and disadvantages of passive and active treatment systems

Passive Treatment	
Advantages	**Disadvantages**
○ There is no need for mechanical or electrical equipment. ○ No hazardous chemicals are added to these systems. ○ Lower operating costs and low maintenance. ○ They appear natural and aesthetic, and they may provide habitat for plants and wildlife.	○ Treated water might not comply with the standards ○ Poor designs can cause systems to fail. ○ Limited to treating water with low acidity. ○ Require large surface land to construct.
Active Treatment	
Advantages	**Disadvantages**
○ Treatment is much more effective than using passive treatment. ○ Systems are more adaptable and can handle any acidity or acid load. ○ They can cope with higher water discharges.	○ They require electrical power ○ Skilled manpower is required for the active treatment of plants. ○ Expensive operating costs. ○ Hazardous chemicals are added to these systems.

3 METHODS AND MATERIALS

3.1 Introduction

The methods used in achieving the objectives of the study are outlined in this chapter. Observations made and measurements taken in the study area are described. This chapter describes sample collection, sample storage procedures, the Dispersed Alkaline System (DAS) design concept, and the analytical techniques used to characterize water.

Identifying the best option for treatment was dependent upon several factors including initial water chemistry (pH, acidity, acid load, and metal concentrations), expected or intended water quality objectives, flow rates, site logistics and economics. The financing mechanism was a key consideration for water treatment, and both capital and operational costs were considered. While cost and ease of implementation are important considerations, the chemistry and volume of the acid water should ultimately influence the choice and viability of the specific technology. The selection of a suitable passive treatment system was done with the aid of the periodic table for passive treatment developed by Gusek and Waples (2009) and the flow chart, as adopted from Hedin (1994). Based on the periodic table for passive treatment, Fe, Al and As can be treated by both anaerobic and oxidising passive systems, whereas Mn can only be treated using oxidising systems. Sulfate can also be potentially removed by means of anaerobic systems through microbial reactions. The DAS system was chosen as its practical for setting up on abandoned mine sites and is associated with low cost of implementation, operation and maintenance. Such conventional treatments have been tried and tested in many parts of the world with their performance and effectiveness in acid water remediation differing in longevity and success from one place to another.

The study aims to assess the constructed system's ability to remove/reduce potentially toxic metals and sulphates in water to meet South African water quality guidelines (SAWQG) for domestic use and South African national drinking standards (SANS 241:2015) standards. Monitoring in the DAS system was carried out every second week before the system was vandalized.

Following field research, the disused Douglas Colliery mine was equipped to run a passive treatment pilot plant to remediate contaminated water from the underground mine.

Preliminary water samples collected indicated that the quality of the water was characterised by pH levels ranging between 2.5 to 4, and EC levels ranging from 162.4 to 290 shown in Table 7 below. TDS levels in water can reduce the quality of potable surface and groundwater supplies, rendering the water unfit for domestic and industrial uses. Primary data in the research study were collected through undertaking fieldwork investigations.

Secondary data were collected through desktop studies which involved the reviewing of existing geological information, technical reports, journals and previous environmental studies conducted around the defunct mine.

Biweekly water sampling was used to determine the quality of water before and after it entered the DAS system due to the availability of project funds. The water quality of the influent was then compared to that of the effluent as an indicator of the performance of each system. SAWQG (1996) domestic and SANS 241 (2015) domestic standards were also used to compare effluent quality.

3.2 Study area

3.2.1 Description of the study area

Douglas Colliery is located in the Witbank Coalfield of Mpumalanga Province in the Highveld Region. The Olifants River Catchment is defined by two quaternary catchments Klipspruit and Blesbokspruit (Vermeulen *et al.*, 2005). Douglas Colliery is located 2 km northeast of the Witbank Central Business District and operated as an underground mine using the bord and pillar method (Vermeulen *et al.*, 2005) (see Figure 13).

Douglas Colliery was considered a derelict and ownerless mine as per DMR's (2009) definition. The little to no rehabilitation in the derelict mine has led to the old underground tunnels being flooded which eventually decant and then discharges into the adjacent Brugspruit River, a tributary of the Klipspruit River (Van Niekerk *et al.*, 2001) in the Olifants River basin. In this area, the part of the Olifants River basin is made up of two quaternary catchments the Klipspruit and the Blesbokspruit (Vermeulen *et al.*, 2005). The Douglas Colliery mining site is also characterised by islands of subsided grounds which are evidence of failed pillars due to spontaneous combustion of the coal in the old mine workings (Hobbs *et al.*, 2008).

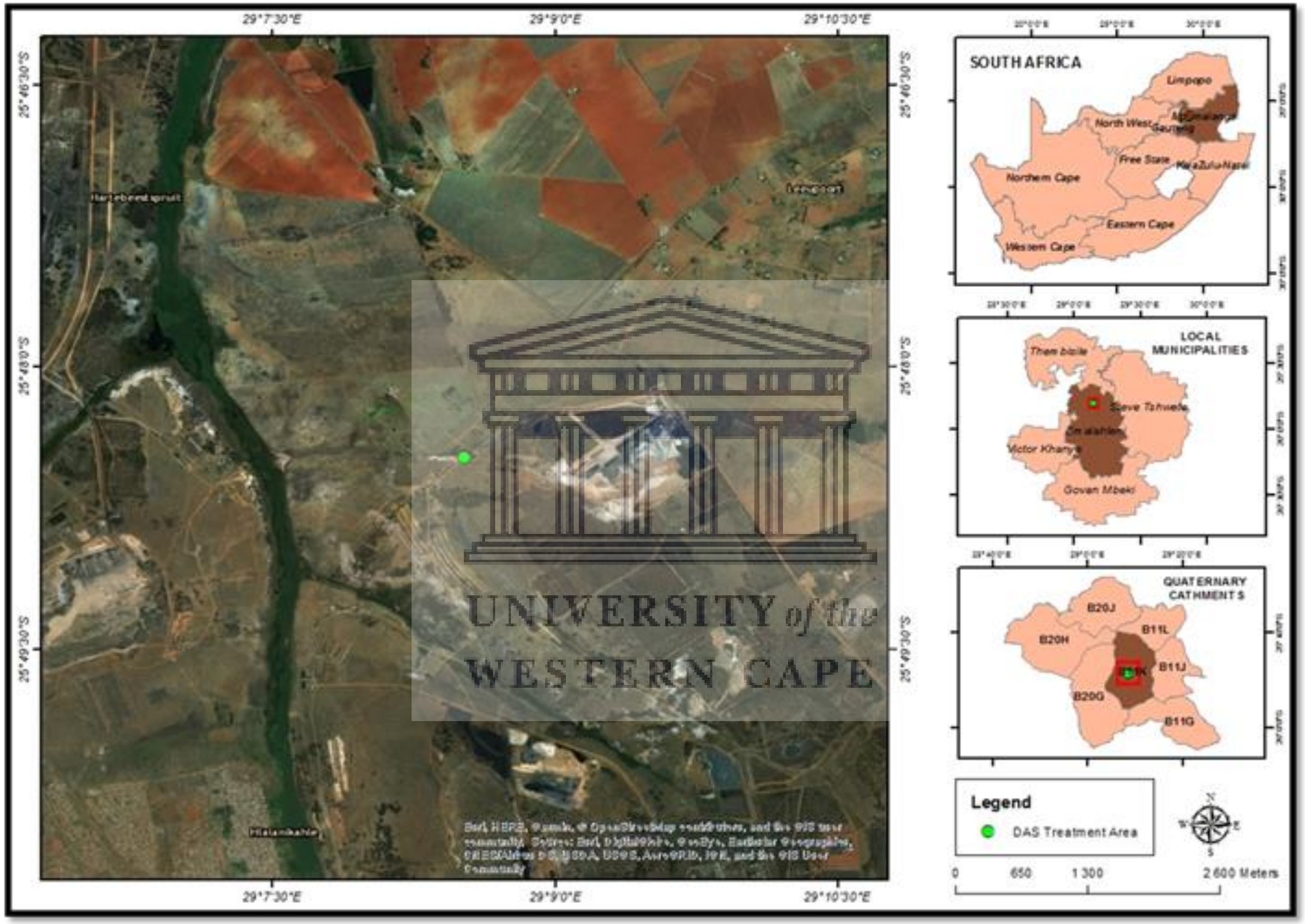


Figure 13: Locality map showing the area of study in Mpumalanga Province.

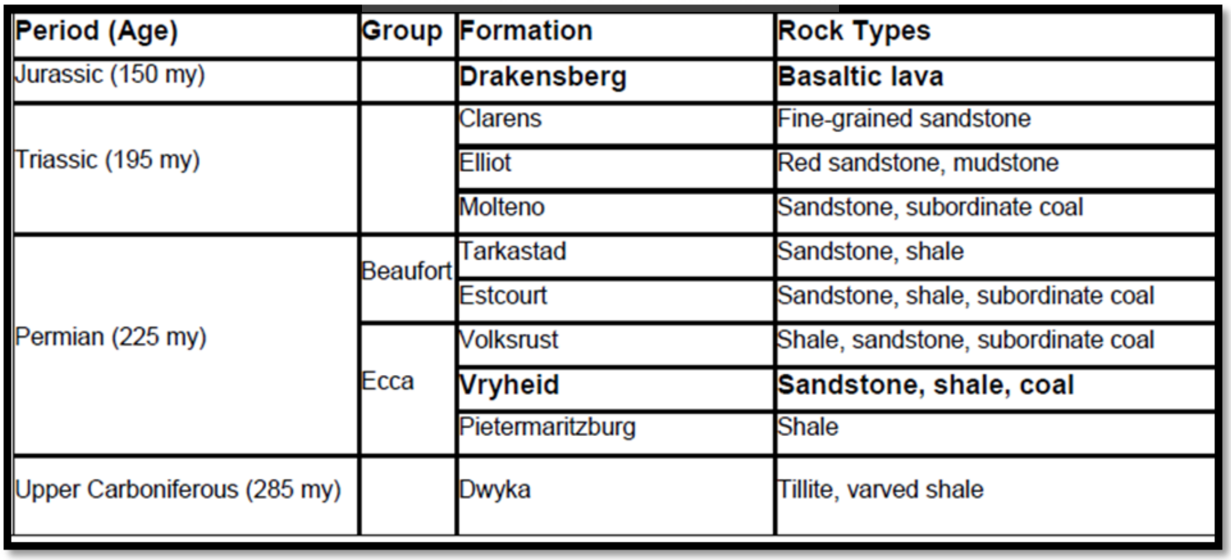
3.2.2 Geological setting of the area

The Witbank Coalfield is located within the northern part of the Karoo Basin and contains the major coal deposits in South Africa. (Hobbs *et al.*, 2008). According to a study done by Mahanyele (2010), the Witbank Coalfield resembles a basin feature that extends from the Western side of Brakpan through to the east of Belfast towns.

As given in Table 2 the coal-bearing strata of the Witbank Coalfield are hosted within the Permian aged Vryheid Formation of the Ecca Group (Bullocl and Bell, 1997). The coalfield contains numerous post-Karoo age dolerite sills and dykes, as well as rocks from the Ecca Group's Vryheid Formation that cover most of the area (Grodner, 2002). The Vryheid Formation and the Dwyka Group, which make up the majority of the Karoo Supergroup in the study area, are made up of sandstone, carbonaceous shale, siltstone, and minor conglomerate (Cairncross, 1989).

The uppermost arenaceous sandstone in the study area is highly weathered and the weathered zone together with topsoil can reach depths of up to 12 m below the surface at some places, especially in the higher laying ground and it becomes thinner in lower laying areas owing to erosion and the intensity of weathering that reduces with depth.

Table 2: Simplified stratigraphic column for the Karoo Supergroup (derived from Cairncross, 2001)



Period (Age)	**Group**	**Formation**	**Rock Types**
Jurassic (150 my)		**Drakensberg**	**Basaltic lava**
Triassic (195 my)		Clarens	Fine-grained sandstone
		Elliot	Red sandstone, mudstone
		Molteno	Sandstone, subordinate coal
Permian (225 my)	Beaufort	Tarkastad	Sandstone, shale
		Estcourt	Sandstone, shale, subordinate coal
	Ecca	Volksrust	Shale, sandstone, subordinate coal
		Vryheid	**Sandstone, shale, coal**
		Pietermaritzburg	Shale
Upper Carboniferous (285 my)		Dwyka	Tillite, varved shale

The Witbank Coalfield is bounded in the north by the Karoo Group's limit and is located in the paleo valley known as the Vischkuil Valley (Smith and Whittaker, 1986). The coal-bearing Ecca Group of the Karoo Sequence sediments in this coalfield were deposited on pre-Karoo paleo-topographic terrain, which had a significant impact on the characteristics and distribution of the coal seams (Jeffrey, 2005a).

As shown in Figure 14, the Dwyka formation is unevenly distributed across the area, being thicker in the paleo valleys and thinner to absent over the paleo high ground. Diamictites, poorly sorted grit and some Dwyka formation shales protrude unconformably from the basement.

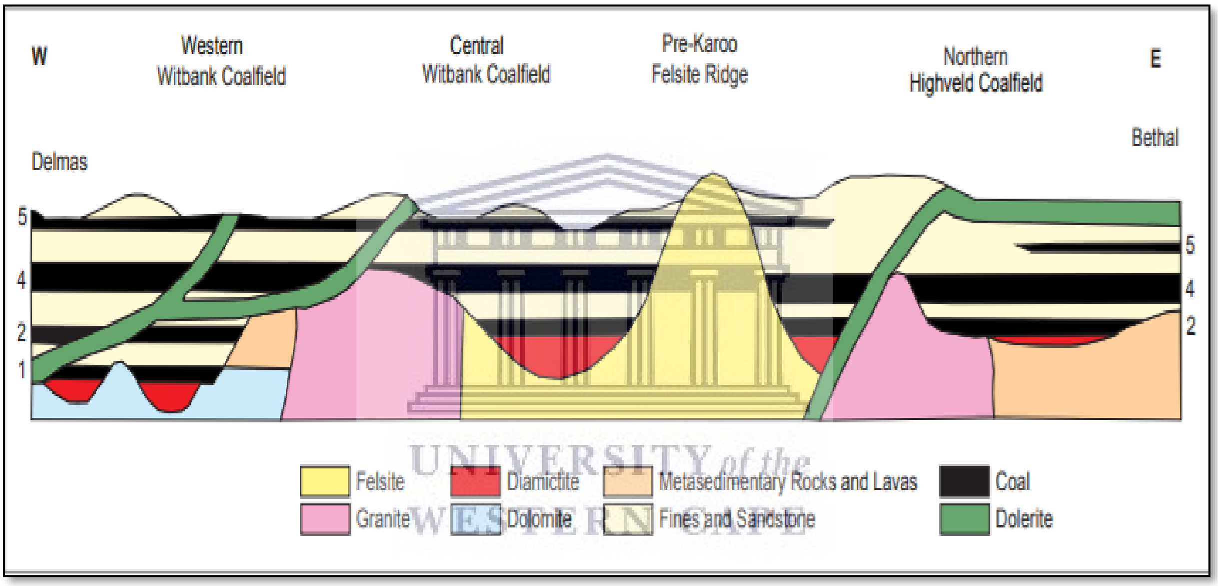


Figure 14: The effects of the Palaeo-topography on the Witbank coal seams (Keaton Energy Holdings,2016)

The sedimentary divisions of the Witbank Coalfield represent a continuous basin-fill sequence deposited after post-glacial warming (Vermeulen and Usher, 2006). Witbank is located near the Karoo Basin's northern limit, where the sediment thins out and the Vryheid Formation rests unconformably on the Transvaal Supergroup, the Waterberg Group, and volcanic rocks associated with the Bushveld Igneous Complex. (Figure 15).

The Witbank coalfield's northern margin marks the northern limit of the Permian Karoo Supergroup sediments, which include the Ecca Group. As a result, the coal seams on the northern edge of the coalfield are relatively shallow.

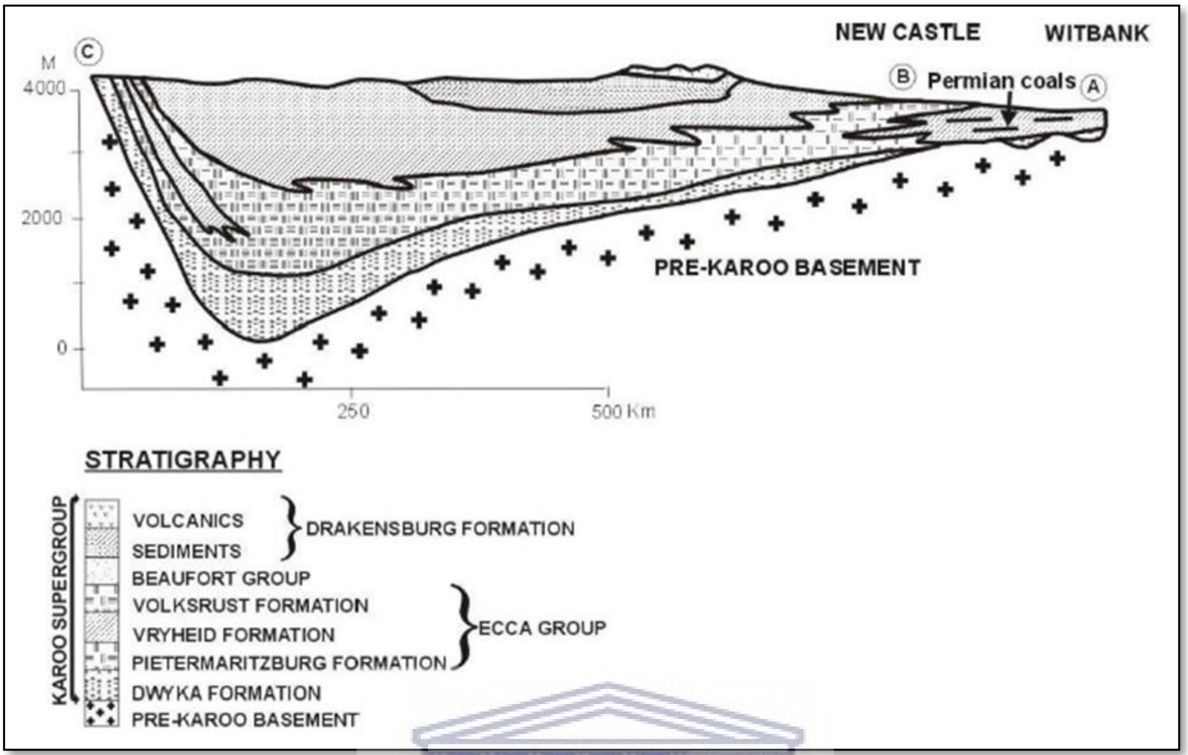


Figure 15: Cross-Section through the Karoo Basin showing the tectonic and stratigraphic position of the coal-bearing Vryheid Formation (Derived from Cadle *et al.*, 1990)

3.2.3 Climate

Monthly rainfall data obtained from the Witbank (SAWB gauge number 0515412 2) station and combined with rainfall data supplied by Golder Associates (2016b), is presented in Figure 16. The Witbank station receives less than 533 mm of rain per year, according to data from the weather station, with the majority of the rain falling during the summer (

Figure 16). The Witbank area lies within the South African Highveld moderate eastern plateau zone. Witbank receives the lowest rainfall in winter and the highest in summer (October to April). As shown in Figure 17 below, the average daily maximum temperature in the area ranges from 15.2°C in June to 25.8°C in January. The region gets the coldest during July when the temperature drops to 4°C on average during the night.

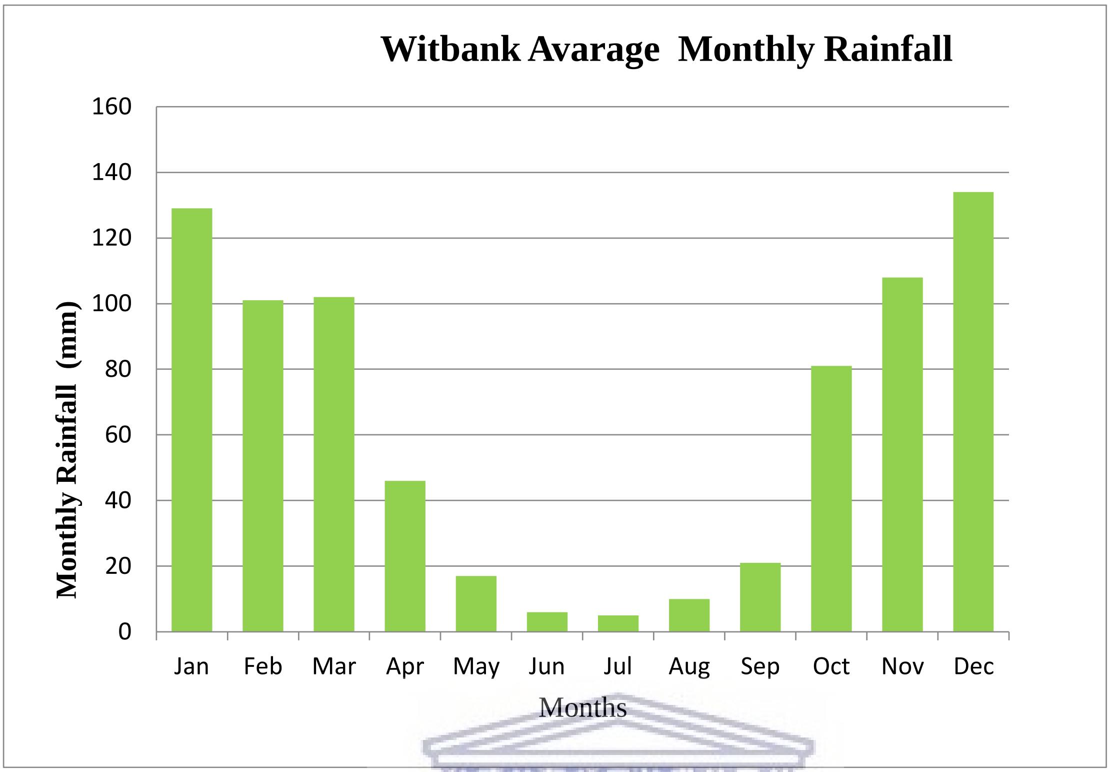


Figure 16: Graph showing the average rainfall of the Witbank (South African Weather Services, 2009)

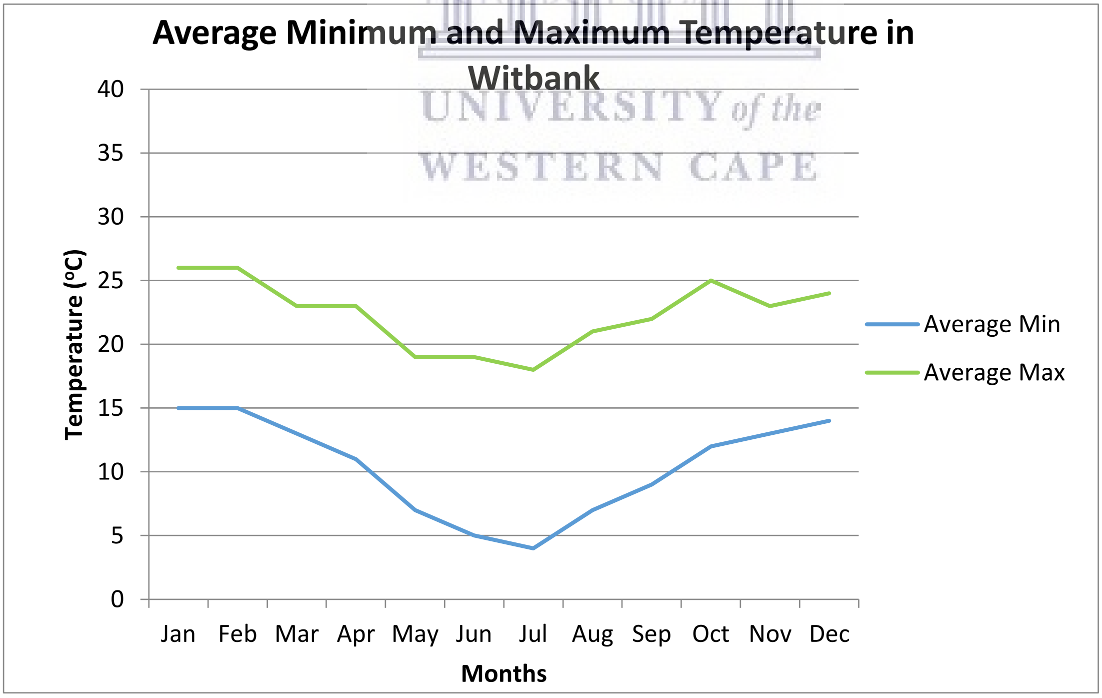


Figure 17: Graph showing the Average temperature in Witbank

3.2.4 Land-use

The study area is located within the B11 and B11K tertiary and quaternary drainage regions of the Upper Olifants River system. The main human activities in the area are farming and the mining of the Witbank Coalfield, which is one of the country's largest coal-producing regions (Figure 18). The abundance of coal reserves in the area has also prompted the construction of power plants in the province. In the south, vanadium and chrome processing plants are also present. This land is largely used for grazing by small subsistence farmers within the catchment and water from the Brugspruit and Klipspruit rivers are utilized for irrigation purposes.

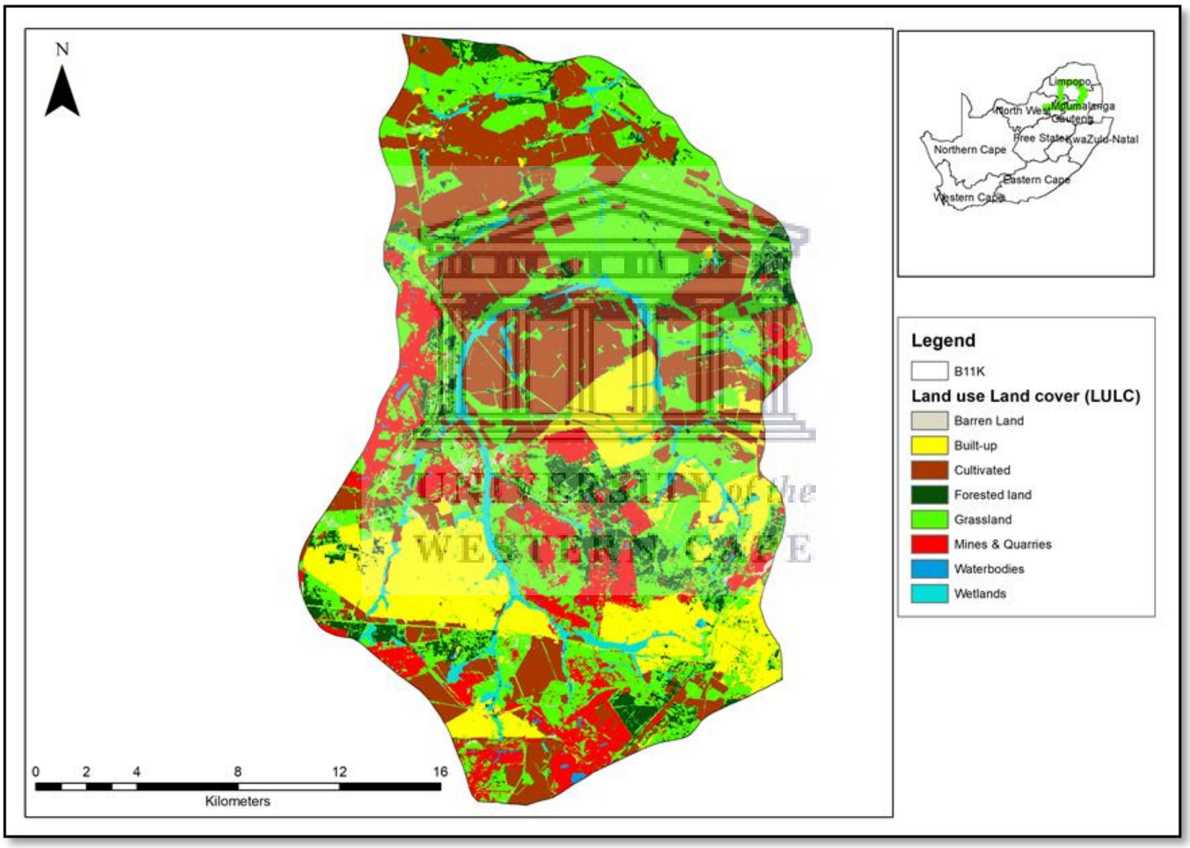


Figure 18: Map showing the Land use and land cover in the study area.

Livestock from the nearby farms and settlements rely on the polluted streams for drinking water. Vegetation in some locations shows severe degradations especially close to the decanting points due to high sterilisation of soil by contaminated mine water. Areas of disturbance or subsidence are marked by large concentrations of alien vegetation species namely the Black wattle tree and Eucalyptus (Bluegum tree) and these species cover most of the study area.

3.2.5 Surface Water Quality

Stream water quality in the Witbank coalfield has deteriorated over the past 20 years, as a result of seepage and discharge of mine water (DWAF, 1999). The study area is located within the Olifants River basin, in the Upper Olifants Water Management Area's B11 and B11K tertiary and quaternary catchments (WMA). The main drainage feature of the catchment is the Klip River which drains northwards onto the Olifants River with the Blesbokspruit and Klipspruit as the two major tributaries.

The seepage of AMD from the Douglas mine has decimated vegetation in some areas and wiped-out aquatic flora and fauna in the Brugspruit and nearby streams. Brugspruit is a tributary of the Klipspruit that drains headwaters of the catchment (Wates, 2002). The Brugspruit originates from the Southwest of Witbank and it flows in a Northerly direction towards the Klipspruit (Figure 19). Even though attempts have been made by the Department of Water and Sanitation (DWA) at treating the water at the Brugspruit plant, most of the decanting AMD is not captured for treatment in the plant.

Coal mining has a significant impact on the hydrological cycle in the Upper Olifants catchment. Mining, industrial, and residential development have all had a significant impact on the catchment's water resources of the catchment (WMB,1997). Studies undertaken by DWAF (2001), indicate that the water quality for domestic use in the Klipspruit has been rendered unfit for any user including potable and irrigation use.

Metal hydroxides and oxyhydroxides, particularly those of iron and aluminium, coat fish gills, suffocating the fish.

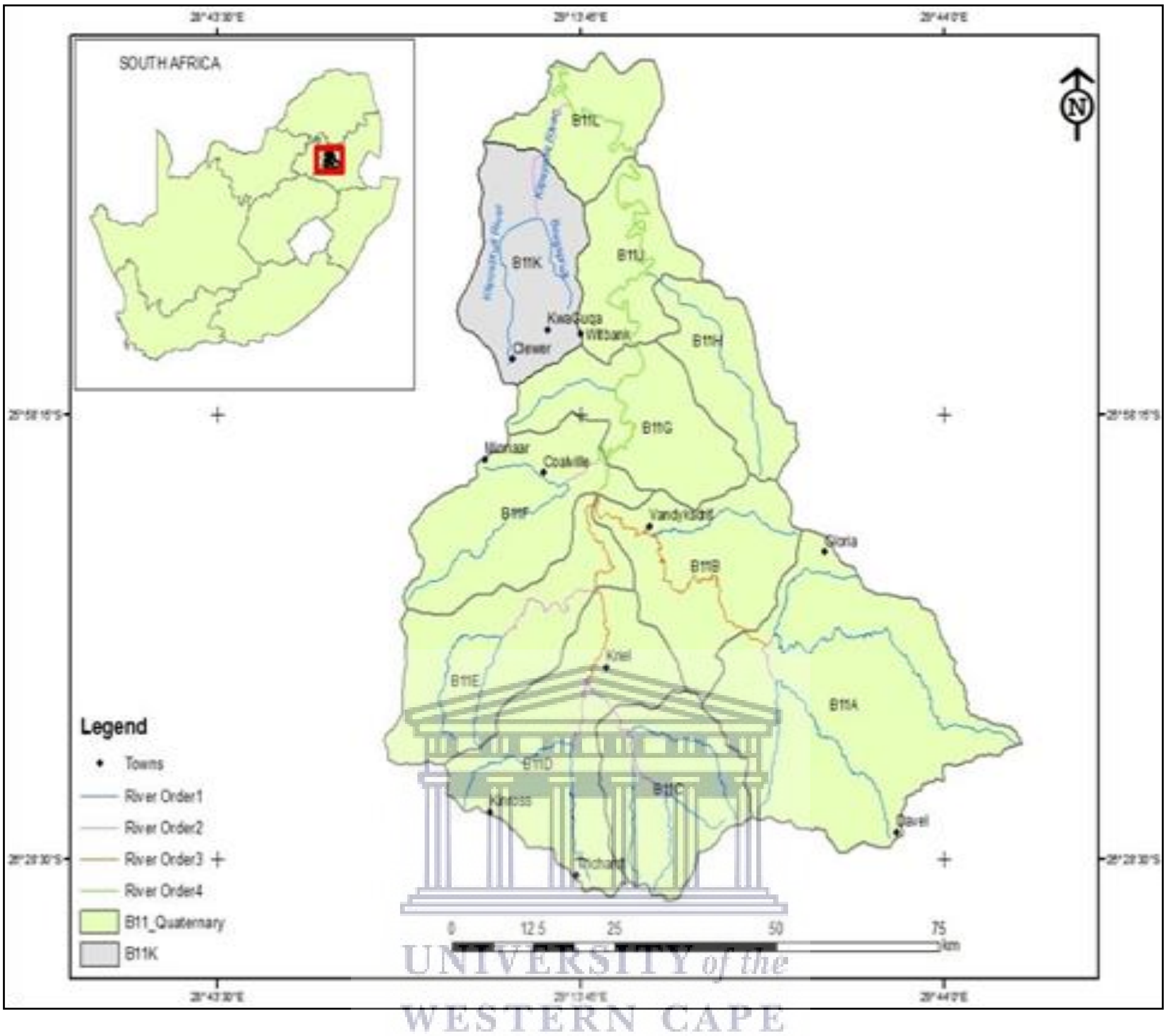


Figure 19: Spatial distribution of rivers in the study area (adapted from Kgari *et al*., 2016)

3.2.6 Site selection

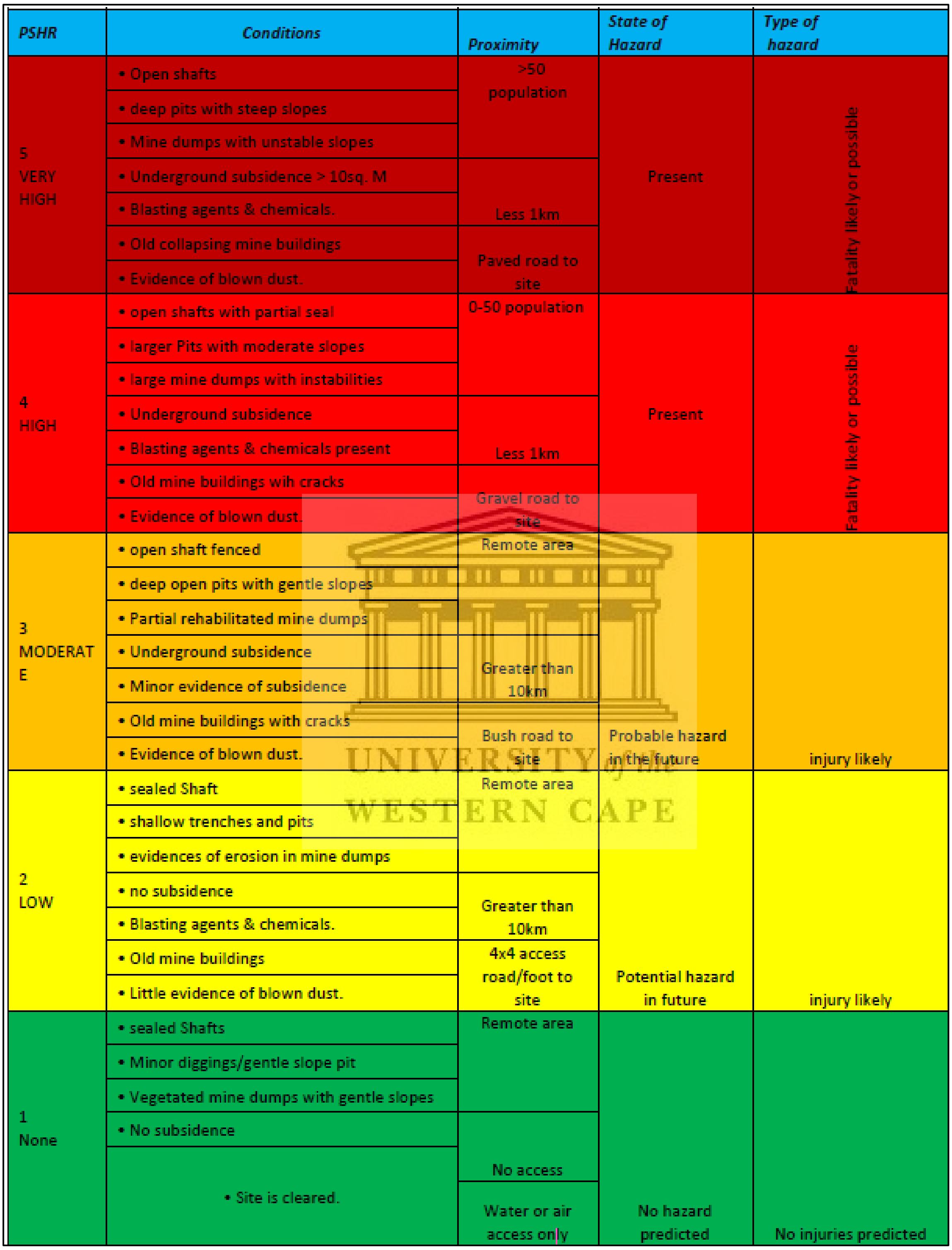
As part of the Derelict and Ownerless (D&O) mines, project scope preliminary investigations and sampling were undertaken in the Witbank Coalfields to identify contaminated sites as well as to identify contaminants of concern in the eMalahleni mining area. Focus was placed on the defunct mines that are flooded and currently decanting polluted water into the surrounding water resources. Based on the risk ranking matrix developed by the DMR and CGS, the Douglas Colliery was identified as one of the derelict coal mines requiring urgent attention. The site was chosen as it poses environmental and physical harm to the nearby settlements and water resources. The water discharged is generally characterised by a typical reddish colour (caused by precipitated ferric hydroxide see Figure 21 and Figure 22) low pH, and concentrations of Fe, Al, Mn, and Sulphates that are two to three orders of magnitude higher than the acceptable limits of the standards (see Table 7). The study area is located in an area characterised by collapsed underground works as a result of underground mine fires (Coetzee, 2013).

Gusek and Waples (2009) developed a passive treatment periodic table based on Hedin (1994), and this was used in the selection of a suitable passive treatment system. Based on the periodic table for passive treatment, Fe, Al, and As can be treated by both anaerobic and oxidising passive systems, whereas Mn can only be treated using oxidising systems.

The decision to implement the pilot plant was also supported by the risk-ranking matrix done onsite as shown below (Figure 20). A Risk-ranking matrix can be defined as a qualitative approach of acquiring abundance data about many derelict and ownerless mines over a large area within a short space of time. The main aim of the ranking matrix is to obtain baseline information of both the public health and safety and environmental impacts associated with the derelict and ownerless mines. Information collected on each site is critical in making well-informed decisions such as ranking the risk of physical conditions and chemical conditions on each site in order to make an informed prioritising for rehabilitation.

Public safety is related to mine workings such as shafts, pits, adits and stopes. The risk evaluation of physical condition on all mine features must take into consideration the nature and size, conditions of the mine feature, proximity to settlement and conflict to current and future land use. Guidelines for public safety hazard rating were created based on conditions that need to be considered to ensure public safety from derelict and ownerless mines (Table 3).

Table 3: Guidelines for Public Safety Hazard Rating (PSHR)



PSHR	*Conditions*	*Proximity*	*State of Hazard*	*Type of hazard*
5 VERY HIGH	• Open shafts	>50 population	Present	Fatality likely or possible
	• deep pits with steep slopes			
	• Mine dumps with unstable slopes			
	• Underground subsidence > 10sq. M	Less 1km		
	• Blasting agents & chemicals.			
	• Old collapsing mine buildings	Paved road to site		
	• Evidence of blown dust.			
4 HIGH	• open shafts with partial seal	0-50 population	Present	Fatality likely or possible
	• larger Pits with moderate slopes			
	• large mine dumps with instabilities			
	• Underground subsidence	Less 1km		
	• Blasting agents & chemicals present			
	• Old mine buildings wih cracks	Gravel road to site		
	• Evidence of blown dust.			
3 MODERATE	• open shaft fenced	Remote area	Probable hazard in the future	injury likely
	• deep open pits with gentle slopes			
	• Partial rehabilitated mine dumps			
	• Underground subsidence	Greater than 10km		
	• Minor evidence of subsidence			
	• Old mine buildings with cracks	Bush road to site		
	• Evidence of blown dust.			
2 LOW	• sealed Shaft	Remote area	Potential hazard in future	injury likely
	• shallow trenches and pits			
	• evidences of erosion in mine dumps			
	• no subsidence	Greater than 10km		
	• Blasting agents & chemicals.			
	• Old mine buildings	4x4 access road/foot to site		
	• Little evidence of blown dust.			
1 None	• sealed Shafts	Remote area	No hazard predicted	No injuries predicted
	• Minor diggings/gentle slope pit			
	• Vegetated mine dumps with gentle slopes			
	• No subsidence	No access		
	• Site is cleared.	Water or air access only		

Public health is related to exposure to mine waste materials and water discharge from old mine workings. Mine wastes can negatively impact human health within measurable proximity to derelict and ownerless mines. Table 5 summarises the factors used to rate the public health effects of derelict and ownerless mines. The health impacts associated with derelict mines can be classed according to short-term and long-term effects. Short-term health effects are experienced almost within a short period of exposure to mine waste. Short-term health effects can be due to a high degree of exposure to pollution. Long-term health effects are recognised after a long period. Long-term health effects can be due to a low degree of exposure to pollution. Other cases are due to the nature of the commodity i.e. in the case of 7 asbestos mines. Health effects due to exposure to asbestos fibres are normally experienced after 10-20 years.

Environmental contamination in derelict and ownerless mines is related to mine waste. Environmental degradation rating includes assessment of potential contamination, nature and extent of the contamination. Environmental components investigated include soil, surface water, groundwater and air. The assessment process includes observation of all evidence of stress in vegetation and aquatic life, surface staining of soil and presence of precipitates, presence of salts on surface water, evidence of soil erosion in tailings and waste dump, evidence of oxidation and evidence of erosion by air. Guidelines for environmental degradation hazard rating of derelict and ownerless mines are summaries in Table 4. Assessment details the possibilities of pollution to occur, the potential source of pollution, targeted receptor/s, the extent of the pollution and the sensitivity of the receptor/s. Site-specific conditions such as geology, topography and climatic conditions must be considered during environmental degradation rating.

Illegal mining is common in historic sulphide metalliferous, gold, diamond and PGMs mines. Illegal mining hazard rating estimates the degree of illegal mining based on the number of illegal miners, different ethnic groups, the proximity of the mine to human settlement and the mining methods used.

The method of scoring mine features based on their risk, magnitude and proximity to settlement is crucial in making decisions for setting priorities. The guidelines for the hazard rating system were based on the principles of risk management.

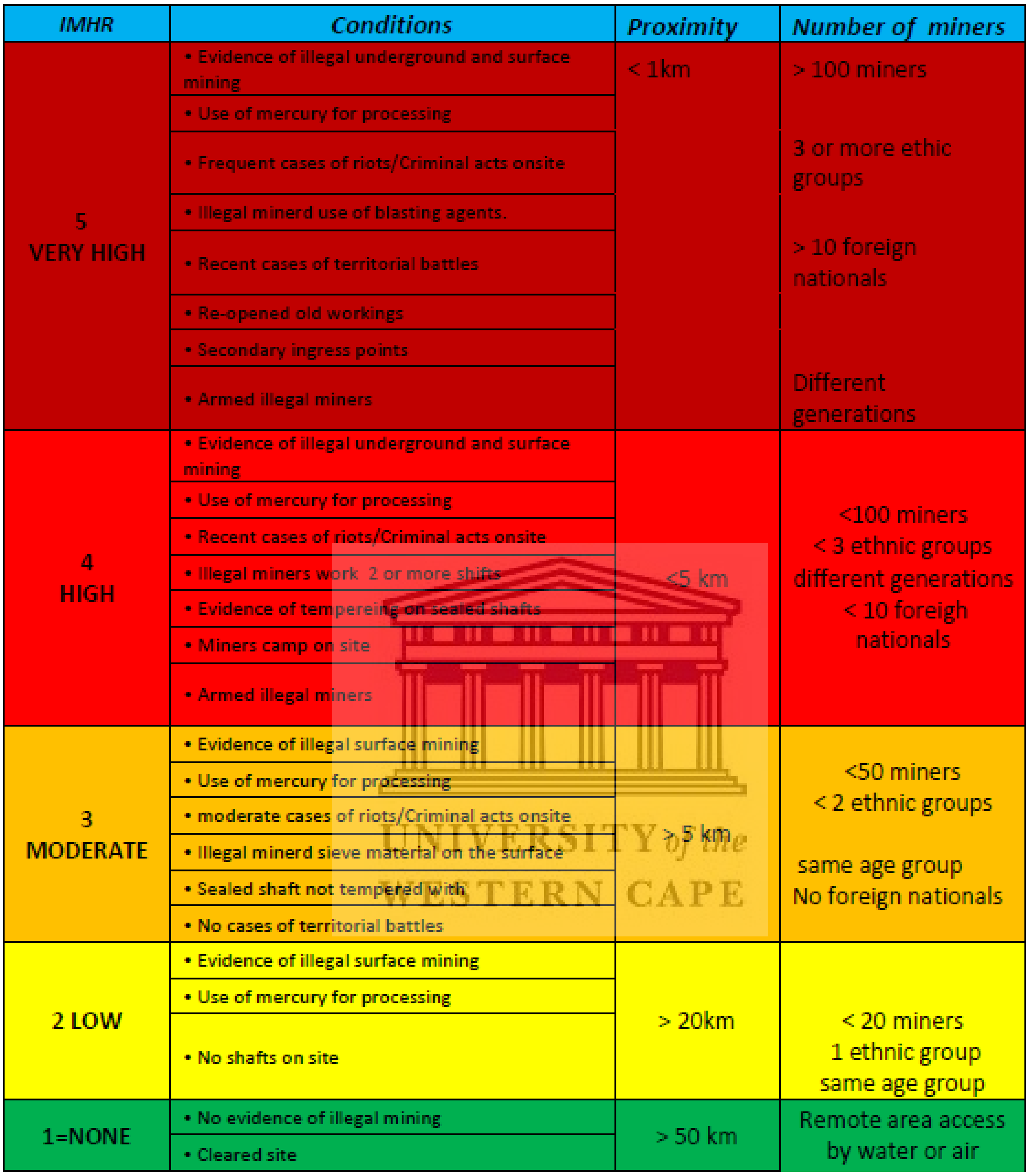
Table 4: Guidelines for Environmental Degradation Hazard Rating (EDHR). (Modified from Sares *et al.*, 2009)

EDHR	Conditions	Scale
5 VERY HIGH	• Contamination off-site is severe.	Proven impacts over 10 km
	• High concentration of metals and salts (, XRF, ICP-MS)	
	• High concentration of Potential Harmful Elements (XRD, XRF, ICP-MS results)	
	• Evidence of stressed aquatic life in receiving stream.	
	• Mine discharge with low pH (<4).	
	• Mine discharge with extremely high conductivity (>1500 microsiemens per centimetre - µS/cm).	
	• High volume of mine discharge to surrounding environment/ stream.	
	• Observable precipitates on mine site and surrounding environment.	
	• Very large sulphide rich mine dumps with evidence of severe erosion (XRF, XRD).	
4 HIGH	• Moderate contamination off-site.	Proven or potential impacts over between 1-10 km
	• Mine water with low pH (<5).	
	• Mine water with high conductivity (>1000 µS/cm).	
	• Moderate flows of mine discharge to relative to the receiving stream.	
	• Moderate concentration of metals and salts.	
	• Moderate to abundant precipitates at the mine and surrounding enviironmnet.	
	• Large sulphide-rich mine dumps with evidence of moderate erosion (XRF, XRD).	
	• Moderate concentration of Potential Harmful Elements (XRD, XRF, ICP-MS results).	
3 MODERATE	• Little contamination off-site/ pollution over a small area	Potential impacts between 100m-1km
	• Mine discharge with low pH (<5.5).	
	• Mine discharge with moderate conductivity (>600 µS/cm).	
	• Poor-quality water with no flow.	
	• Low concentration of metals and salts	
	• low concentration of Potential Harmful Elements (XRD, XRF, ICP-MS results)	
	• Minor observable precipitate on site.	
	• Very large dumps with no sulphides and little or no erosion.	
	• Small and moderate-sized sulphide-rich dumps or tailings piles with evidence of moderate erosion (XRF, XRD).	
2 LOW	• Mine discharge with slightly acidic pH (<6.5).	Potential impacts between 0-100m
	• No evidence of contamination	
	• Mine discharge with slightly elevated conductivity (>400 µS/cm).	
	•Low concentration of Potential Harmful Elements (XRD, XRF, ICP-MS results)	
	• Low concentration of metals and salts	
	• Mine discharge of moderate quality water	
	• No evidence of precipitate.	
	• Small to moderate-sized sulphide-rich dumps or tailings piles with little evidence of erosion (XRF, XRD).	
1 NONE	• No mine discharge.	No impact identified
	• Low concentration of metals and salts	
	• Mine discharge with high quality water (ICP-MS).	
	• Small dumps distant from surface water with little or no evidence of erosion and no sulphides.	

Table 5: Guidelines for Public Health Hazard Rating (PHHR)

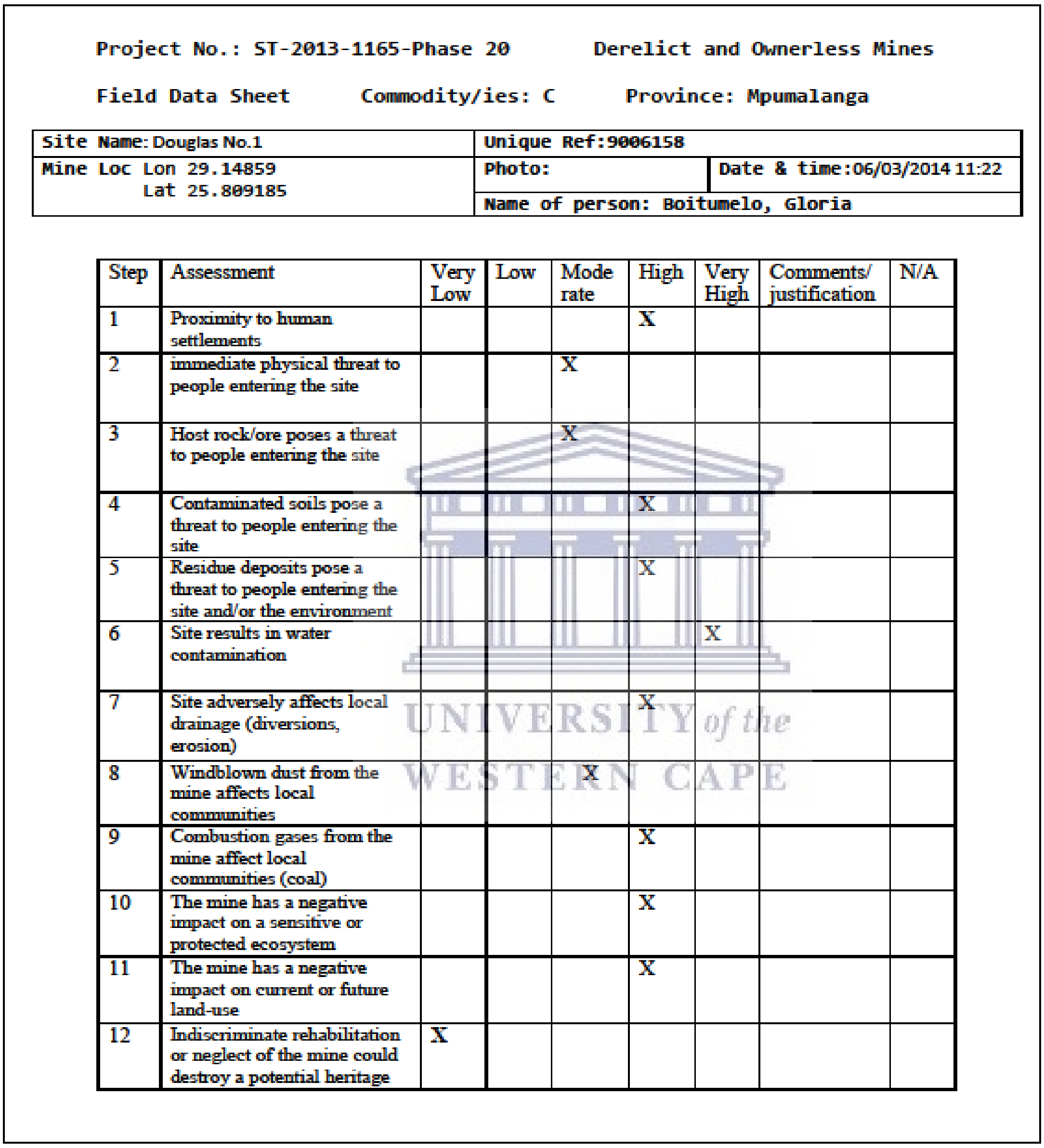
PHHR	Conditions	Proximity	Exposure
5 VERY HIGH	• Exposed mine dumps	Less 1km	> 50 population
	• Evidence of windblown dust		
	• High concentration of Potential Harmful Elements(PHEs) (XRD, XRF)		
	• Evidence of stressed aquatic life in receiving stream.		
	• Mine discharge with low pH (<4).		
	• Extreme contamination off-site		
	• High volume of mine discharge to surrounding environment/ stream.		
	• Observable precipitates on mine site and surrounding environment.		
	• Very large dumps with evidence of severe erosion		
4 HIGH	• Moderate contamination off-site.	Less 1km	0-50 population
	• Mine water with low pH (<5).		
	• Mine water with high conductivity (>1000 µS/cm).		
	• Moderate flows of mine discharge		
	• Moderate concentration of metals and salts.		
	• Evidence of wind blown dust		
	• Large dumps with moderate erosion		
	• Moderate concentration of PHEs (XRD, XRF).		
3 MODERATE	• Little contamination off-site/ pollution over a small area	Greater than 10km	Remote area access by bush road
	• Mine discharge with low pH (<5.5).		
	• Mine discharge with moderate conductivity (>600 µS/cm).		
	• Poor-quality water with no flow.		
	• Low concentration of metals and salts		
	• low concentration of Potential Harmful Elements (XRD, XRF)		
	• Minor observable precipitate on site.		
	• Very large dumps with little or no erosion.		
	• Moderate evidence of wind blown dust		
2 LOW	• Mine discharge with slightly acidic pH (<6.5).	Greater than 20km	Remote area access by 4x4 / foot
	• No evidence of contamination		
	• Mine discharge with slightly elevated conductivity (>400 µS/cm).		
	•Low concentration of Potential Harmful Elements (XRD, XRF)		
	• Low concentration of metals and salts		
	• Mine discharge of moderate quality water		
	• Rehabilitated dumps.		
	• Small tailings piles with little evidence of erosion (XRF, XRD).		
1 NONE	• No mine discharge.	Greater than 50km area	Remote area access by water or air
	• Low concentration of metals and salts		
	• Mine discharge with high quality water (ICP-MS).		
	• Rehabilitated dumps no evidence of erosion and no sulphides.		

Table 6: Guidelines for Illegal Mining Hazard Rating (IMHR)



IMHR	*Conditions*	*Proximity*	*Number of miners*
5 VERY HIGH	• Evidence of illegal underground and surface mining	< 1km	> 100 miners
	• Use of mercury for processing		
	• Frequent cases of riots/Criminal acts onsite		3 or more ethic groups
	• Illegal minerd use of blasting agents.		> 10 foreign nationals
	• Recent cases of territorial battles		
	• Re-opened old workings		
	• Secondary ingress points		Different generations
	• Armed illegal miners		
4 HIGH	• Evidence of illegal underground and surface mining	<5 km	<100 miners < 3 ethnic groups different generations < 10 foreigh nationals
	• Use of mercury for processing		
	• Recent cases of riots/Criminal acts onsite		
	• Illegal miners work 2 or more shifts		
	• Evidence of tempereing on sealed shafts		
	• Miners camp on site		
	• Armed illegal miners		
3 MODERATE	• Evidence of illegal surface mining	> 5 km	<50 miners < 2 ethnic groups same age group No foreign nationals
	• Use of mercury for processing		
	• moderate cases of riots/Criminal acts onsite		
	• Illegal minerd sieve material on the surface		
	• Sealed shaft not tempered with		
	• No cases of territorial battles		
2 LOW	• Evidence of illegal surface mining	> 20km	< 20 miners 1 ethnic group same age group
	• Use of mercury for processing		
	• No shafts on site		
1=NONE	• No evidence of illegal mining	> 50 km	Remote area access by water or air
	• Cleared site		

A small-scale Dispersed Alkaline System (DAS) was adopted and modified following Rotting *et al.*, (2008) to ensure that the treatment system could reliably treat acid mine drainage under field conditions and ensure that the discharged effluents met the SAWQG (1996) Domestic use and SANS 241 (2015) domestic standards.



Project No.: ST-2013-1165-Phase 20 **Derelict and Ownerless Mines**

Field Data Sheet **Commodity/ies: C** **Province: Mpumalanga**

Site Name: Douglas No.1	**Unique Ref:**9006158
Mine Loc Lon 29.14859 Lat 25.809185	**Photo:** **Date & time:**06/03/2014 11:22 **Name of person: Boitumelo, Gloria**

Step	Assessment	Very Low	Low	Mode rate	High	Very High	Comments/ justification	N/A
1	Proximity to human settlements				X			
2	immediate physical threat to people entering the site			X				
3	Host rock/ore poses a threat to people entering the site			X				
4	Contaminated soils pose a threat to people entering the site				X			
5	Residue deposits pose a threat to people entering the site and/or the environment				X			
6	Site results in water contamination					X		
7	Site adversely affects local drainage (diversions, erosion)				X			
8	Windblown dust from the mine affects local communities			X				
9	Combustion gases from the mine affect local communities (coal)				X			
10	The mine has a negative impact on a sensitive or protected ecosystem				X			
11	The mine has a negative impact on current or future land-use				X			
12	Indiscriminate rehabilitation or neglect of the mine could destroy a potential heritage	X						

Figure 20: Douglas Colliery risk ranking matrix

Table 7: Physico-chemical water quality parameters measures of the study area

Physico-chemical parameters	Units	Decanting water	DWAF Guideline
EC	(uS/cm)	1624	≤ 70
TDS	(mg/L)	2760	≤ 450
pH		2.5	5 - 9.7
Aluminium (Al)	(mg/L)	111	0 -0.15
Sulphate SO_4^{2-}	(mg/L)	1590	0 - 200
Iron (Fe)	(mg/L)	495	0 – 0.1

Figure 21: A photograph showing source of mine effluent and evidence of secondary mineralisation

Figure 22: Aeration pond with typical red/orange colour due to iron hydroxide.

3.3 DAS system design concept

The design of the constructed DAS was essentially driven by the hydrochemistry of the mine water. The volume and concentrations of potentially harmful metals in mine water were also critical in determining the size, type of technique, and land area required for treatment. The pH levels were also important in determining the type of treatment elements required. The mine discharges between 0.17 to 3 ML/d of mine water contributing to the pollution of the water resources in the upper Olifants River basin. The influent is controlled to maintain inflow rates ranging between 1-2 L per minute into the DAS system. The influent flow is kept at that rate to obtain a residence time of at least 24 hours in the DAS tanks.

Caraballo and Rötting (2009) describe the DAS treatment systems as systems based on flow through a reactor filled with non-reactive materials, typically of coarse grading, mixed with a reacting alkaline material. In the current study, the DAS system used coarse wood chips mixed with a fine-grained alkaline material, such as limestone or magnesia (Rotting *et al.,* 2008). The wood chips allow for high permeability in the system, reducing clogging, and the fine limestone's small grain sizes provide a large reactive surface area, allowing it to be consumed before precipitates coat it (Macias *et al.*, 2012). To reduce clogging, organic matter in the system was used to control the redox state of the system. This method was developed by Rotting *et al.* (2008) as it addresses issues related to clogging or coating of reactive materials in passive treatments systems.

Previous attempts were made by the DWAF to construct an active treatment system in 1997 at a cost for R 26.5 million (DWAF, 1997). The treatment system sought to protect the water resources in the catchment from impacts of AMD by treating the mine discharge water to non-harmful qualities. However, the treatment plant failed because of various factors such as poor consideration of the volume of water to be treated, shortage of staff to operate the plant, lack of maintenance and high costs of operation of the plant.

The DAS system was chosen because it is feasible to implement and it utilises cheap materials that are readily available in the nearby vicinity. The system was designed to treat low flowing net acidic mine water.

The DAS treatment system was constructed between the source and channel leading to Brugspruit River. The DAS system has 4 treatment stages namely the aeration pond, DAS 1, DAS 2 and DAS 3 as described in the following sections. Substrate materials were chosen based on chemical and physical properties to efficiently support the effectiveness of the system.

3.3.1 Source

Water decanting from the old mine workings has a low pH, high EC, high TDS and a high concentration of potentially hazardous elements e.g Fe, Mn (Dube *et al.,* 2018). A concrete opened channel was built to improve the oxygenation of the impacted mine water.

Evidence of secondary mineralisation of ferrous iron was noted from the source to the aeration pond (Figure 21). Approximately 2 L of effluent water per minute was measured at the derelict mine during the time of the study.

3.3.2 Aeration pond

The constructed aeration pond has a large surface area for the mine water to encounter as much atmospheric air as possible. This keeps dissolved gases from mine water from escaping into the atmosphere. The exposure of the mine water to atmospheric oxygen further removes dissolved metals through oxidation which are later removed by filtration or flotation. The constructed aeration pond converted the Fe in a ferrous state to ferric (Figure 22). Other trivalent metals such as Al and Ferric iron are expected to precipitate in this step (Pulles *et al.,* 2001).

3.3.3 DAS 1 (Limestone and wood shavings)

The water is diverted through a 50 mm pipe from the aeration pond to the 4.3 m^3 DAS 1 reactive tank. The mine effluent is fed into the DAS 1 through a polyethene pipe from the bottom of the tank (Figure 24 and Figure 26). This reactive material has a high porosity (50%) that is required to maintain hydraulic conductivity and prevent clogging caused by passive treatment systems that precipitate solids within the porous space of the reactive material. The defunct mine discharges 2 L of mine water per minute which is equivalent to 2880 L per day. The retention period in each DAS unit was 24 hours. This retention period was set to 24hrs to allow for metal oxidation and hydrolysis, allowing potentially harmful elements like Fe^{2+}, Al^{2+}, and Mn^{2+} to precipitate and be physically retained.

A 50 cm layer of limestone in the form of calcium carbonate (with at least 85 % $CaCO_3$) with less than 0.1 mm particle sizes was put in the DAS 1 reactive tank. The layer of limestone was then overlain by a 30 cm layer of wood shavings.

Figure 23: Wood shavings materials used in the study

Figure 24: Field-scale set-up of the DAS system implemented at the Douglas site, Mpumalanga.

3.3.4 DAS 2 (Manure and wood shavings)

The DAS 2 reactive tank contains a 1 m layer of cow manure and a 1 m layer of wood shavings. This manure served as an agent to reduce sulphates were reduced to hydrogen sulphide through the microbial processes. The microbes creating anaerobic conditions in the DAS tank consume oxygen in the tank. According to Wildman *et al.* (1993), microorganisms found in the organic material aids in oxidation and reduction reactions. The manure layer's primary function is to remove oxygen from the water via microbial aerobic respiration.

The manure in the reactive tank encourages permeability and uniform flow. It also helps in stabilizing the substrate and maintaining microbial populations. The chemical equation for sulphide conversion from sulphate is shown below :

$$SO_4 + 2\ C_{organic} + 2\ H_20 + \text{microbial activity} \rightarrow H_2S + 2HCO_3$$

The chemical equation for sulphide conversion from sulphate ………………………………..(Equation 17)

Robert and McVay (2009) reported that the hydrogen sulphate gas is colourless but pungent therefore can be easily detected by the sense of smell.

3.3.5 DAS 3 (Waterwheel and carbon fibres)

Water in this reactive tank undergoes aeration to further precipitate potentially harmful elements such as Fe and Al that were not removed through the initial three steps. The carbon fibre wheels acted as a surface area where microbes could attach to and multiply, which is expected to aid in the breakdown of heavy metals, which are remaining in the system as shown in Figure 25 below.

Figure 25: DAS 3 fitted with carbon fibre wheels

Rotation of the carbon wheels was achieved by gravity-fed water running the waterwheel, which is in turn connected to an axel where the circular contactor discs are attached. According to Yin *et al.*(2007), “activated carbon is an amorphous solid consisting of micro crystallites with a graphite lattice, and are non-polar, and highly porous”. The highly carbonaceous material can remove potentially harmful metals via the complexation or electrostatic attraction of metal ions.

3.3.6 Sampling Layout

Sampling was conducted for 4 months before the system was vandalised. Water samples were collected bi-weekly in 5 designated monitoring stations (Table 8). The portable field meter was calibrated on-site using the provided standards, and the main physicochemical parameters were measured in the field.

Table 8: Sampling points along the seepage stream from the decanting point

Sampling Points	Location
Source	Decanting Point
Pre-treatment	Aeration Pond
DAS 1	1st reactor tank inlet into the system
DAS 2	2nd reactor tank after DAS 1
DAS 3 (Effluent)	Settling pond and outlet point

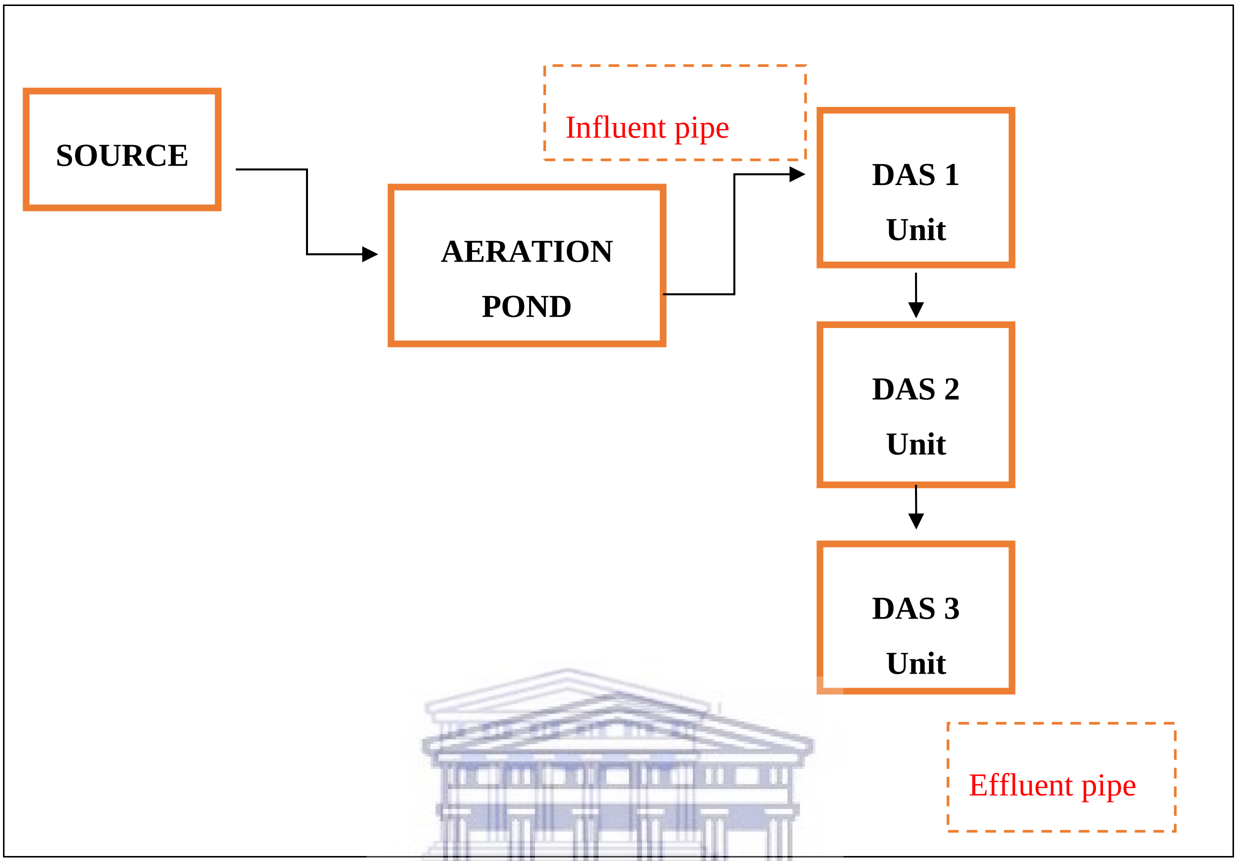


Figure 26: Schematic representation of the DAS arrangement used in a defunct mine in eMalahleni, Mpumalanga.

3.3.7 Methods of analysis

3.3.7.1 Water Quality Comparison

DWAF (1996) defines the term water quality as the physical, chemical, biological and aesthetic properties of water that determine its fitness for a variety of uses and for protecting the health and integrity of aquatic ecosystems. The concept of water quality is directly related to or dependent on the intended use of water. Different uses of water such as drinking, irrigation or recreation require different criteria (Cordoba et al., 2010). Traditionally, water quality has been assessed by comparing experimentally measured parameter values to pre-existing standard guidelines. The water chemistry data from the DAS system were compared to water standards to determine the system's efficiency in reducing metal loads and whether the quality of the treated water released meets the SAWQG domestic water use (DWAF,1996) and SANS 241:2015 drinking standards.

3.3.7.2 Field Measurements

Physical parameters measurements of water were conducted *in-situ* to avoid any alterations due to different environments while in storage containers and during transportation as well as in the laboratory. Throughout the study, water samples were collected from five monitoring stations. A Universal Multiline P4-SET3 field meter (WTW, Germany) equipped with a pH combined electrode with an integrated temperature probe (Sen Tix 41), standard conductivity cell (Tetra Con 375), was used to record *in-situ* pH, electrical conductivity (EC), Total Dissolved Solids (TDS), temperature, and dissolved oxygen (DO) (Sen Tix ORP).

Before the measurements, the pH meter was calibrated using three buffers with pH 4, pH 7 and pH 10. The conductivity probe was also calibrated before measurements, using 0.1 M KCl standard solution. Water samples were collected in three sets of 250 ml high-density polyethene (HDPE) sample bottles per sampling point for the analyses of alkalinity, anions and cations (Figure 27). During sampling, bottles were rinsed with deionized water before they were filled and air-tight capped for prevention of possible oxidation during storage.

Figure 27: a) Equipment utilised during sampling of water in the field b) Universal Multiline P4-SET3 field meter (WTW Germany) and polyethene sampling bottles

All samples were filtered *in-situ* with 0.45 µm filters and cation samples were acidified immediately using 3 mL of nitric acid (HNO_3) to keep metals dissolved and to prevent them from precipitating. Samples collected for anion analyses were also filtered on-site with 0.45

µm filters but were not acidified. The above sampling procedure was carried out as outlined by Weaver *et al.* (2007).

The sample bottles were then labelled with a permanent marker and stored in a cooler box filled with ice before transportation and further analysis at the Council for Geoscience Chemistry Laboratory.

3.3.7.3 Discharge measurement

Because of consideration of contamination loads and discharge volume, discharge measurement is critical for the proper design of passive treatment systems (Hedin *et al.*, 1994a). Flow measurements were conducted at sources of mine water discharge, using the Bucket-and-stopwatch methods. Bucket-and stopwatch. This method uses a container or bucket of known volume to fill water while the time-to-fill is estimated using a stopwatch (Figure 28). PIRAMID Consortium (2003) and Wolkersdorfer (2008) recommended that the procedure be repeated three times to reduce uncertainties. The overall discharge is then estimated as follows:

Determination of water flow rate using bucket and stopwatch method

$$Q = V/\Delta t \quad \text{(Equation 18)}$$

Where Q is the discharge (as $m^3 s^{-1}$), V is the volume of the container (m^3) and Δt *is the average* time in seconds to fill the container (s).

Figure 28: Mine discharge estimation using the bucket and stopwatch method.

3.3.7.4 Laboratory Measurements

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Ion Chromatography (IC)

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Ion Chromatography (IC) were used to analyse the collected water samples for metals and anions, respectively. The concentrations of the elements were then compared to the South African water quality standards (DWAF, 1996).

The samples were analysed for the following: Magnesium (Mg), Calcium (Ca), Sodium (Na), Copper (Cu), Chloride (Cl), Sulfate (SO_4), Iron (Fe), Aluminium (Al), Nickle (Ni), Chromium (Cr), Arsenic (As), Lead (Pb), Manganese (Mn), and Zinc (Zn). Table 9 summarizes the field and laboratory water analyses conducted during the experiment and the justification of these analyses.

Table 9: Field and laboratory water analyses conducted

ANALYSES TYPE	PARAMETERS	JUSTIFICATION
On-site Analysis	pH	Acidity and alkalinity of the water
	TDS	Measure the concentration of total dissolved solids
	EC	Measure the ability of a solution to conduct electricity
Laboratory Analysis	ICPMS	Measure the concentration of potentially harmful elements
	IC	Measure the concentrations of common anionic constituents

Ionization of aqueous samples at high temperatures in an argon plasma is used in the ICP-MS analysis technique. Concentrated ions are accelerated through a material stream toward detectors that measure isotope masses (Robinson, 1990). While conventional ICP-MS techniques can detect elements at concentrations of a few parts per billion to parts per million, recently developed and improved guidelines enable detection at concentrations per trillion. Since a sample only needs to be ionized once, ICP-MS analysis enables the rapid, simultaneous, or sequential determination of multiple elements in a single analytical session, though interference from plasma gases, background radiation from other elements, and interferences from larger excesses of single elements are the analytical technique's primary disadvantages (U.S.EPA, 1986).

X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF)

Before use, the limestone was characterized using X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) methods for mineral and element (traces and major) identification and concentrations.

3.3.8 Statistical Analysis

3.3.8.1 Descriptive analysis

The study generated the maximum, minimum, mean, and standard deviation of the determinants using descriptive statistical analysis of the water sample variables. Descriptive statistics were used for the assessment of the magnitude and direction of changes in the treated water, and comparisons were made with accepted standards. The target water quality ranges for SANS 241:2015 drinking and SAWQG domestic water use standards (1996) were used as criteria for comparing with the mean concentrations of trace elements and water parameters. Histograms were used for graphical analysis of the data, and to determine whether the data were normally distributed. When using multivariate statistics, it is important to make sure that the data is normalised. Parameters are transformed to increase their normal distribution which is preferred for optimal results and reliable interpretation.

3.3.8.2 Correlation Analysis

To characterize and quantitatively understand the relationship between various metals and water quality parameters, Pearson's product-moment correlation analysis was used to determine the possible relationships and calculate the correlation between the considered variables (pH, EC, Fe, Al, Ni, Cr, Cu, As, Pb, Mg, SO4, Mn, TDS, Ca and Zn) for the selected sampling points. The relationships between the variables are represented by the correlation coefficient (r). A strong relationship between two variables is indicated by a correlation coefficient near +1 (for a positive relationship) or -1 (for a negative relationship), whereas no relationship is indicated by an r-value of zero. A positive correlation indicates that the two move in the same direction, with a +1.0 correlation when they move in tandem. A negative correlation coefficient tells you that they instead move in opposite directions.

3.3.8.3 Multivariate Analysis (MVA)

In general, multivariate analysis (MVA) is a statistical procedure for the analysis of data involving more than one type of measurement. MVA also relates to the solving of problems where more than one dependent variable is analysed simultaneously with other variables. Multivariate analysis techniques are therefore extremely useful for analysing data containing many interacting variables. These techniques produce simple-to-understand results. The term "multivariate data" refers to observations made on multiple variables for multiple samples (sample vectors or individuals).

Multivariate statistical techniques have been widely applied to aid in the resolution of Multivariate statistical techniques have been widely applied to aid in the resolution of environmental issues and to provide insight into interactions between natural processes (Singh *et al.,* 2004; Shrestha and Kazama, 2007). These techniques may enable the identification of potential pollution sources affecting water systems, making them an effective tool for ensuring reliable water resource management and quickly resolving pollution issues.

Techniques for multivariate analysis were applied to the data collected in this study to determine clear and “hidden” relationships as well as controlling parameters in the DAS system using IBM’s SPSS Statistics 20 software. To aid in the identification of important components or factors accounting for many of the variances in the DAS system, factor and principal component analyses were used (Ouyang *et al*., 2006; Shrestha and Kazama 2007). In assessing the water quality, variations in discharge and concentrations from the inflow and outflow at a source were undertaken.

3.3.8.4 Factor Analysis (FA)

Factor analysis (FA) is a statistical procedure for identifying inter-relationships between a large number of variables (Yu et al., 2003). Factor analysis works by detecting sets of variables that correlate highly with each other. These variables may then be condensed into a single variable. Data analysts will often carry out factor analysis to prepare the data for subsequent analyses. Thus, FA generates several combinations of observed variables, each of which represents an independent factor. The factors are a summary of the patterns of correlation between the variables. The first factor accounts for the majority of the variance in the data, and each succeeding factor accounts for less variance (Tabachnick and Fidell, 1996).

Principal Components was selected as the extraction method. The total number of factors/components generated from a factor analysis indicates the total number of possible sources of variation in the data and the ranking of these factors is ordered according to their importance. The first factor or component represents the most important source of variation in the data while the last factor is the least important process contributing to the chemical variation (Yidana et al., 2008). Factor loadings on the factor loadings tables are interpreted as correlation coefficients between the variables and the factors, they represent how much each variable contributes to the factor (Yong and Pearce, 2013).

Factor analysis was performed using pH, TDS, EC, Al, Fe, Cr, Cu, As, Pb, Ni, Mg, Ca, Zn, SO_4.

3.3.8.5 Removal Efficiency

The nature and composition of the substrate have an impact on the removal efficiency. A paired comparison of the quality of both the influent and effluent water was used. This was applied for both the chemical and physical determinants. The influent from the source, and effluent from the last DAS unit, were used to determine the efficiency rate of the treatment system (Brix, 1997), following the formula below:

$$Efficiency\ Removal\ Precentage = \frac{(Mine\ Water - Effluent)}{Mine\ Water} \text{ X100} \quad \text{……….…..……Equation 19}$$

4 RESULTS AND DISCUSSION

4.1 Introduction

All field and laboratory results are presented in this chapter. This includes data of all samples collected from the source up to the effluent points. Results of the physical and chemical analyses of the mine water samples are presented in APPENDIX 1.

4.1.1 Composition of the reactive material

The mineralogical constituent of the limestone used in the study was analysed using XRD (Table 10). The limestone substrate used contained 80 wt % $CaCO_3$ which served as a buffer. The dissolution of $CaCO_3$ in DAS 1 resulted in the elevation of Ca^{2+} in the system thus elevating the pH of the influent. CaO_3 is the dominant (<40 wt %) major oxide, followed by silica (SiO_2) (<wt 8%). All the other detected/identified trace elements occur in lesser concentrations. $CaCO_3$ is an important buffer/neutralising mineral.

Table 10: Composition of limestone substrate in (as wt %)

Sample	EGU 1064	EGU 1065	EGU 1066	EGU 1067	EGU 1068
SiO_2	8.84	9.79	14.22	10.21	9.22
TiO_2	0.16	0.18	0.25	0.18	0.16
Al_2O_3	1.58	1.71	2.50	1.82	1.71
Fe_2O_3	1.37	1.54	2.31	1.60	1.44
MnO	0.111	0.129	0.092	0.102	0.112
MgO	3.01	3.26	3.96	3.16	3.15
CaO	48.06	46.93	43.45	46.66	47.19
Na_2O	0.02	<0.01	<0.01	0.01	0.03
K_2O	0.05	0.06	0.07	0.05	0.05
P_2O_5	0.022	0.023	0.026	0.022	0.023
Cr_2O_3	0.003	0.003	0.006	0.004	0.003
Lol	36.78	36.43	32.79	36.07	36.56
Total	99.99	100.06	99.68	99.90	99.66
H_2O	4.60	4.28	7.98	4.52	4.20

* Note that **EGU** stands for Environmental Geoscience Unit

4.1.2 Hydrochemical analyses of the mine water, influent and effluent of the treatment plant

The hydrochemical results were compared to the SAWQG standards for domestic water use and SANS 241:2015 drinking standards. Table 11 shows the statistical summary of the DAS system in terms of the mean values and the standard deviations from the average value and compared to water quality guidelines.

Hydrochemical results revealed that the system was able to add a substantial concentration of Ca in the first two weeks of inception. This increase in Ca species was directly proportional to the increase in pH throughout the treatment plant. These recorded results were expected as the dissolution of calcite increases alkalinity thus suppressing some potentially harmful elements. Initially, the decanting mine water contained pH values ranging between 2 and 3 with an average value of 2.8. The pH in the aeration pond had an average of 3.4 and further increased to 5.4 in DAS 1 due to the presence of the limestone substrate. DAS 2 had an average pH of 5.8 with DAS 3 recording an average of 5.

The pH values for DAS 1 and DAS 2 was well within the standard limits set by SAWQG for domestic water use and SANS 241 for drinking purposes. pH concentrations at the source are not permissible for domestic use as per the SANS 241:2015 drinking standard (Table 14). According to the standards, there are no specific health effects associated with pH concentrations above 5, however, deleterious effects occur when the pH concentrations are below 5, as this promotes the dissolution of potentially harmful metals.

The EC recorded at the source ranged between 1.97 to 7.83 mS/cm with a mean value of 4.47 mS/cm. These EC values exceed the 1.7 mS/cm standards limit for domestic use as set by SANS 241:2015 drinking standards. Long-term exposure to high EC in water has been linked to gastrointestinal irritation in humans (Ramesh and Elango, 2012). EC was inversely proportional to the pH. A decline in the concentration of EC was recorded throughout the treatment plant with the effluent recording a mean value of 1.86 mS/cm. The salinity of the water within the system showed an improvement from 3211 mg/L at the source to 1871 mg/L at the effluent.

The ICP-MS results revealed that the total Al was reduced from an average of 293 mg/L at the source to 45.6 mg/L in DAS 3. Total Fe has also reduced from an average of 166 mg/L at the source to 141 mg/L at the effluent. Similarly, As was recorded high at the source with an average of 1.5 and was reduced to 0.5 at DAS 3. SO_4 mg/L was significantly reduced from 2019.0 mg/L at the source to 810.6 mg/Lat DAS3. Ca gradually decreased from the source with 325.9 mg/L and sharply increased at DAS 3 with 677.6 mg/L attributed to the dissolution of the limestone added in DAS 1 and the alkalinity generated from the sulphate reduction in DAS 2.

Fe, Al, As, SO_4 and Ca at the source were non-compliant with the SANS 241:2015 drinking and SAWQG (1996) domestic water use at the source. Most of the potentially harmful elements recorded a decline from the source to the aeration pond and they were further suppressed in DAS 1 and DAS 2 (Figure 36). The histogram presented in Figure 36 shows a positive skewness of Fe and Mn supporting a strong removal of these potentially harmful elements throughout the treatment system.

The increase in Ca concentration recorded in the DAS 3 complemented the increase in pH. These recorded results were expected as the dissolution of calcite increases alkalinity thus suppressing some potential harmful elements.

These findings were earlier hypothesised by Grodner (2002) that the metallic sulphate-rich Witbank Coals possess the potency to generate AMD. Hobbs *et al.,* (2008) echoed similar findings, stating that the AMD promotes the liberation of potentially harmful elements to streams. On-field pH results of the source showed a directly proportional relationship with the EC and TDS. Moreover, acid mine drainage exacerbates the solubility of potentially harmful elements such as Al, As, Cd etc. (Sibiya, 2019). These findings were similar to the results of this study, which recorded low pH values and high concentrations of Al^{2+}, Mg, Mn, Fe and SO_4 at the decanting point. There was an elevation of the pH of the decant water due to the dissolution of $CaCO_3$ by releasing Ca thus resulting in the precipitation of some of these potentially harmful elements. The pH varied between the different endpoints of the DAS system due to temperature variations which affected the water temperature thus affecting the dissolution of the carbonates species.

Table 11: Statistical summary table of the DAS system in terms of the mean values and the standard deviations from the average value

	Source					Pre-treatment					DAS 1					DAS 2					DAS 3				
	Mean	Median	Std. Deviation	Min	Max	Mean	Median	Std. Deviation	Min	Max	Mean	Median	Std. Deviation	Min	Max	Mean	Median	Std. Deviation	Min	Max	Mean	Median	Std. Deviation	Min	Max
Al	293.2	163.8	411.2	59.4	1444.6	60.6	35.4	69.0	0.1	163.7	65.2	49.9	71.2	0.1	163.7	50.8	2.5	80.8	0.3	203.0	45.6	2.5	72.9	0.3	193.0
As	0.5	0.2	0.5	0.0	1.0	0.1	0.1	0.0	0.0	0.1	0.9	1.0	0.3	0.0	1.0	0.9	1.0	0.3	0.0	1.0	1.0	1.0	nd	1.0	1.0
Ca	325.9	355.5	146.6	62.4	526.4	285.1	289.4	153.4	45.7	559.4	262.5	252.9	163.5	45.7	559.4	293.4	383.0	169.1	43.5	446.6	677.6	387.8	1287.5	30.0	4311.7
Cr	nd	nd	nd	nd	0.1	nd	nd	nd	nd	0.1	0.2	nd	0.4	0.0	1.0	0.2	nd	0.4	nd	1.0	0.2	nd	0.4	nd	1.0
Cu	0.1	0.1	nd	0.1	0.2	0.1	0.1	0.1	0.1	0.4	0.2	nd	0.3	0.0	1.0	0.2	0.1	0.4	nd	1.0	0.2	nd	0.4	nd	1.0
Fe	166.7	174.5	107.5	12.0	388.3	111.4	35.1	118.8	14.9	302.0	121.2	71.6	115.8	14.9	302.0	141.5	49.8	161.3	13.3	429.0	141.5	49.8	161.3	13.3	429.0
Mg	288.7	196.6	360.6	38.6	1286.8	29.6	30.0	8.4	19.6	49.5	29.6	30.0	8.4	19.6	49.5	76.6	91.2	39.2	21.6	119.7	72.4	75.1	43.6	15.6	127.9
Mn	145.6	64.4	251.7	9.4	849.8	24.9	21.6	15.7	6.0	56.8	24.1	21.0	16.3	6.0	56.8	20.7	24.5	10.4	5.8	30.9	20.7	24.5	10.4	5.8	30.9
Ni	3.9	2.1	5.7	0.7	20.0	0.8	0.6	0.4	0.5	1.3	0.8	0.8	0.4	0.5	1.3	0.6	0.2	0.5	0.1	1.5	0.6	0.2	0.5	0.1	1.5
Pb	0.4	nd	0.5	nd	1.0	0.3	nd	0.5	nd	1.0	0.9	1.0	0.3	nd	1.0	0.9	1.0	0.3	nd	1.0	0.9	1.0	0.3	nd	1.0
Zn	11.7	7.0	16.5	1.8	58.2	2.5	1.8	2.4	0.9	8.8	2.7	2.4	2.3	0.9	8.8	2.8	0.7	5.0	0.1	16.5	3.1	0.4	5.3	0.1	16.5
SO4	2.019	2.151	0.448	0.95	2.49	1.15	1.05	0.46	0.55	1.95	1.15	1.05	0.46	0.55	1.95	0.85	0.86	0.19	0.48	1.06	0.81	0.82	0.20	0.48	1.06
pH	2.8	3.0	0.4	2.0	3.0	3.4	3.0	0.5	3.0	4.0	5.4	6.0	1.1	3.0	6.0	5.8	6.0	0.4	5.0	6.0	5.0	5.0	0.9	4.0	6.0
TDS	3211.3	3347.0	1119.2	1401.0	5091.0	2676.5	3029.5	945.8	1283.0	3910.0	2230.7	2274.0	524.3	1187.0	3091.0	1348.9	1097.0	445.8	1025.0	2040.0	1871.5	1979.5	256.0	1470.0	2120.0
EC	447.0	479.9	189.5	197.5	783.2	233.1	218.0	64.9	148.5	324.0	197.2	198.8	18.1	149.7	218.0	193.0	192.8	13.5	157.8	205.0	186.2	194.0	24.6	148.5	211.0

Note: pH has no units; SO_4^{2-} was measured in ug/l while all the other cations/anions and trace elements were measured in mg/L while EC is measured in mS/m. * nd – Not detected

Several studies (e.g., Tutu *et al.*, 2008, Rubin *et al.*, 2011, Skoczyńska-Gajda and Labus, 2011) alluded that AMD in streams affects aquatic biota sensitivity to chemical change and reduced pH. Table 12 presents the several impacts associated with some potentially harmful elements.

Table 12: Effects of selected potentially harmful metals

Element	SANS 241:2015	SAWQG limit	Impacts
Al	0.3	< 0.15 mg/L	Alzeheimer disease Neurological disorder Dialysis dementia
Fe	2	< 0.1 mg/L	Eating disorder Appetite disorders Fe mostly affect young children
Mn	0.4	< 0.2 mg/L	neurodegenerative disorder cardiovascular toxicity
Mg	70	100-200 mg/L	Diarrhoea
Zn	5	> 700 mg/L	gastrointestinal irritations, nausea vomiting. renal damage
pH	>5	< 4.0	Diarrhoea Vomiting Gastrointestinal irritations Renal damage

4.1.3 The removal efficiency of the DAS system

The average removal efficacy of the DAS system for each chemical element and major water quality parameter is presented in Table 13. Negative values indicate the addition of concentrations, while positive numbers indicate the removal of concentrations, according to Brix (1997). The removal efficiency is reliant on the physical and chemical properties of the substrate.

Table 13: Removal efficiency of the treatment plant

Parameters	Source	Outlet	Removal efficiency (%)
Aluminium (Al)	293.2	45.6	84%
Arsenic (As)	1.0	0.5	50%
Calcium (Ca^{2+})	325.9	677.6	-107 % (increase in concentration)
Chromium (Cr)	1.5	0.2	86%
Copper (Cu)	2.5	0.2	92%
Iron(Fe)	166.7	141.5	15%
Lead (Pb)	3.6	0.9	75%
Magnesium (Mg^{2+})	288.7	72.4	74%
Manganese (Mn)	145.6	20.7	85%
Nickel (Ni)	3.9	0.6	84%
Sulphates (SO_4^2)	2019	810	59%
Zinc (Zn)	11.7	3.1	73%
pH	2.8	5.0	78% (increase)
EC	4.47	1.86	58%
TDS	3211	1871.5	41%

Note all the chemical determinants are measured in mg/Lexcept for EC, which is measured in mS/cm while pH has no units.

Table 14: Comparison of the National water guidelines of selected hydrogeochemical determinants, with the mean of source and effluent

Determinants	Units	Concentrations			
		Mean		SAWQG (1996) Domestic Water Use	SANS 241 (2015) Drinking water
		Source	Effluent		
Chemical determinants					
Aluminium (Al)	mg/l	293	45.6	0-0.15	0.3
Arsenic (As)	mg/l	1.0	0.5	0-10	0.01
Calcium (Ca^{2+})	mg/l	325	677.6	0-32	150
Chromium (Cr)	mg/l	1.5	0.2	0 - 0.05	0.05
Copper (Cu)	mg/l	2.5	0.21	0-1	2
Iron (Fe)	mg/l	166	141.5	0-0.1	2
Lead (Pb)	mg/l	3.6	0.9	0-10	0.01
Magnesium (Mg^{2+})	mg/l	288	72.4	0-30	70
Manganese (Mn)	mg/l	145	20.7	0-0.05	0.4
Nickel (Ni)	mg/l	3.9	0.6	-	0.07
Sulphates (SO^2)	mg/l	2019	810.6	≤ 200	500
Zinc (Zn)	mg/l	11.7	3.1	0-3	5
Physical determinants					
pH		2.8	5.0	6.9	>5.0 ≤ 9.7
EC	mS/cm	4.4	1.86	≤ 70	1.7
TDS	mg/l	3211	1871	≤ 450	1200

4.1.3.1 pH and EC

The pH values showed a steady increase from the source to the effluent. These recordings are attributed to alkalinity generation due to the dissolution of $CaCO_3$ and reduction of SO_4 by microbial activity which releases bicarbonates. The pH values recorded throughout the system were constant in the first month of the experiment (Figure 29). Lower pH values were recorded after 2 months of operations. The drop in the liberation of Ca^{2+} was due to coating and clogging of the substrate by crystallizing salts forming hardpans. This trend in pH values conforms with electrical conductivity values (Figure 30).

The elevated pH conforms with the precipitation of metals such as Fe, Al and Mn. The concentration of these metals showed a decrease from the source to the effluent. Precipitation and removal of these potentially harmful elements were constant for 1 month (Figure 31; Figure 32; Figure 33; Figure 34; Figure 35). About 84% of Al removal was recorded in the first month of the experiment with Mn at 84%, Fe 15%, SO_4 at 59% and As at 50% (as shown in Table 13).

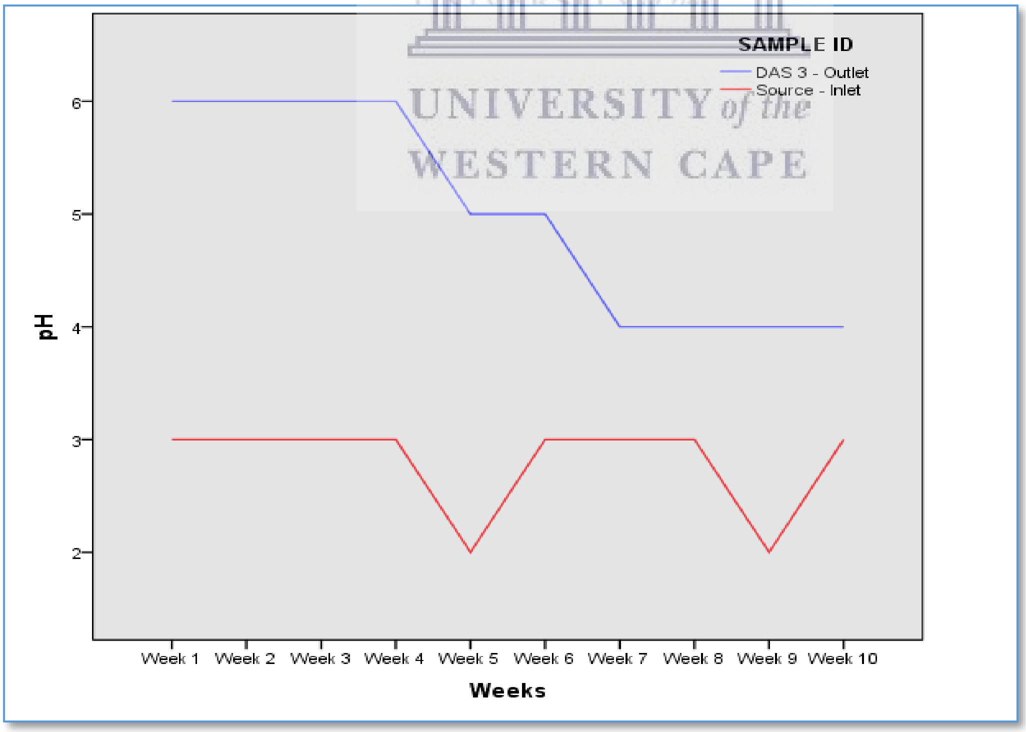


Figure 29: Comparisons of the source and effluent pH.

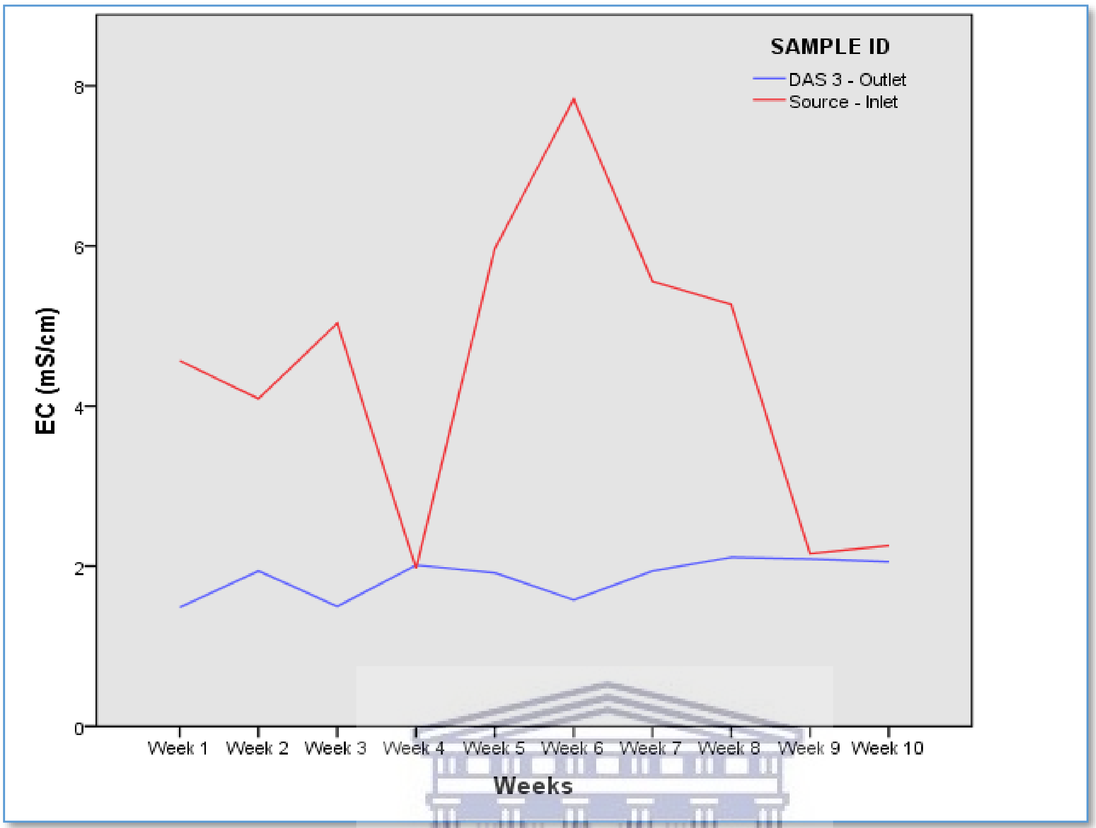


Figure 30: Comparisons of the source and effluent EC.

4.1.3.2 Chemical Determinants

4.1.3.2.1 Aluminium (Al)

A long-time of exposure to Al can cause neurological disorders and Alzheimer's disease. Effects of Al on the aquatic environment are modified by chemical species of Al^{2+} present, life stage of the organism and the pH. The treatment of Al was evident with 84% removal efficiency. Removal is most likely due to oxidation, hydrolysis, and precipitation processes. The removal efficiency of Al was in line with the increased pH in the first two weeks of operations. Al species precipitate in pH waters above 6 and, hence, the white precipitates of Al were observed on top of DAS 2. The decline in the liberation of Ca in week three (3) saw an increase in the Al concentrations (Figure 31). Aluminium hydroxides become unstable at pH levels lower than 5, and this is corroborated by a study done by Nordstrom (1982).

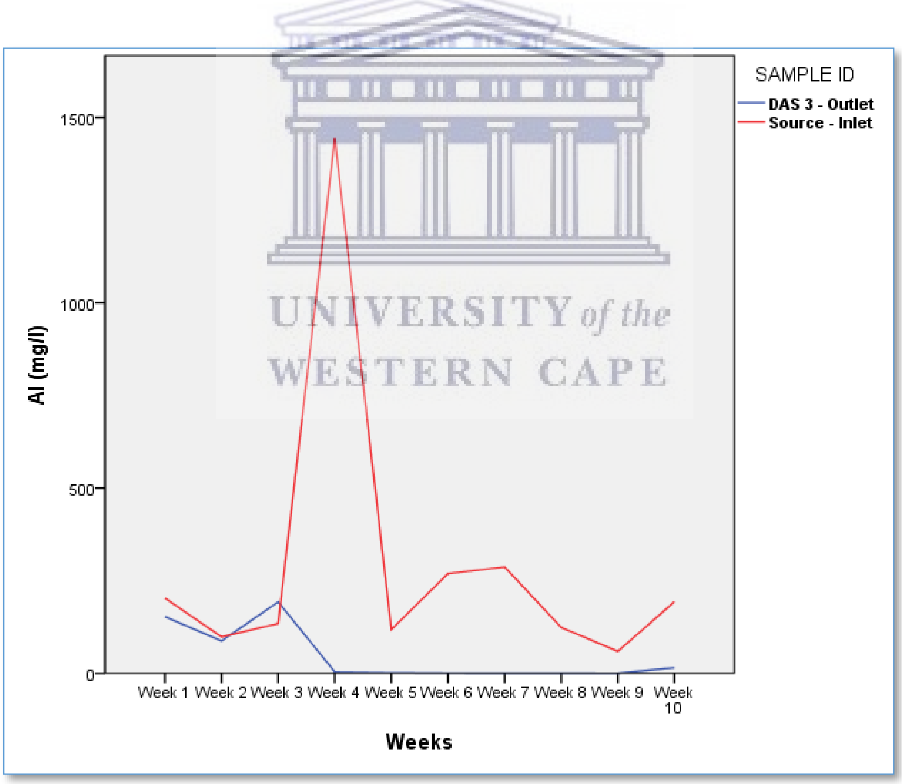


Figure 31: Comparisons of the source and effluent Al concentrations

4.1.3.2.2 Arsenic (As), Chromium (Cr), Copper (Cu) and Lead (Pb)

The trace metals As, Cr, Cu and Pb were below their respective detection limits of <0.01 and <0.001, respectively. The average concentration of these potentially harmful elements at the effluent was found to be above the South African permissible level values reported by DWAF (1996). Carlson and Schwertmann (1981) and Chapman *et al.* (1983) corroborated this when they reported that Fe hydroxides were known to be excellent sorbents of trace metals, (such as Cr, Ni, As and Zn) and as a result can control their mobility, fate and transport in the environment.

4.1.3.2.3 Calcium (Ca)

An increase of Ca was observed between weeks 4 and 5 as compared to the Ca concentration at the source, which was low (Figure 32). The increase is due to the water being in proximity to the limestone mineral in DAS 1. The Ca concentrations was due to the active dissolution of calcite as shown in Equations 20 and 21. The increase in Ca was directly proportional to the pH values. The liberated Ca species from the calcite dissolution was able to neutralise the pH of the decant waters.

$CaCO_3$+2H+ →Ca^{2+}+H_2O+CO_2 ……………………………………………………………………..(Equation 20)

$CaCO_3$+H_2CO_3 →Ca^{2+}+2HCO_3 ……………………………………………………………………..(Equation 21)

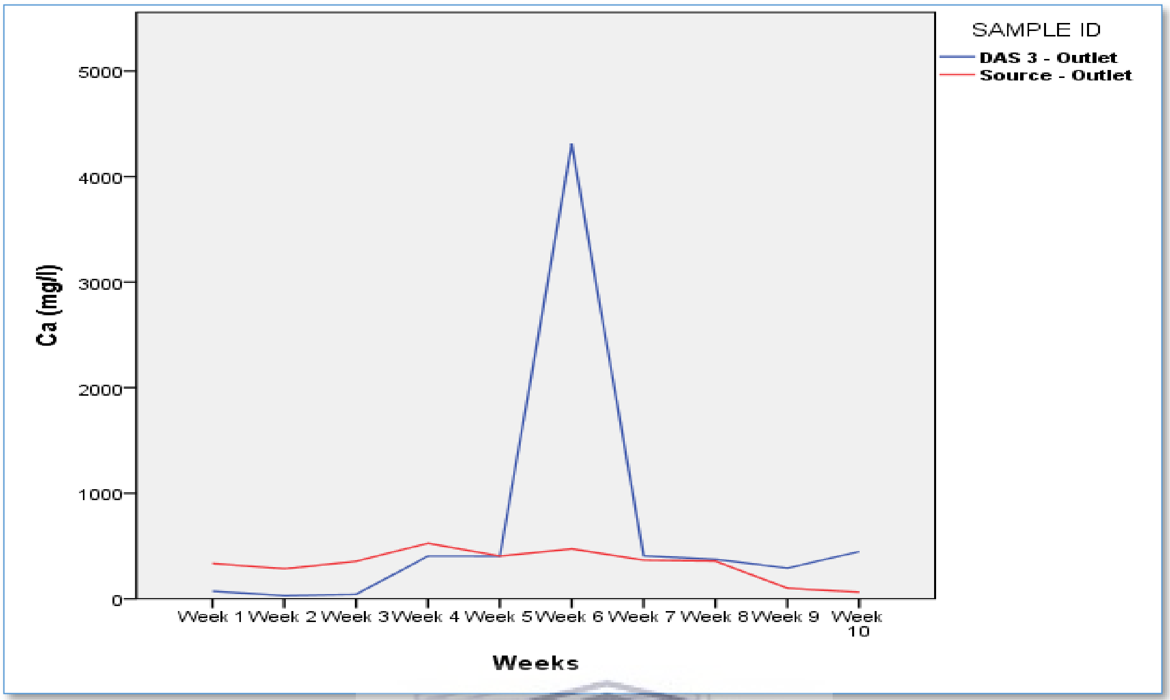


Figure 32: Comparisons of the source and effluent for Ca concentrations.

4.1.3.2.4 Iron (Fe)

The removal efficiency of Fe was relatively low throughout the treatment plant with an overall percentage of 15% (Figure 33). The relative precipitation of Fe species was low due to the presence of a high concentration of Mn species. The Fe concentrations recorded at the effluent exceeded the SAWQG (1996) domestic use standards of 0.1 mg/L. The mine waters bore an average of 166.7 mg/L of Fe and the effluent waters bore an average of 141.5 mg/L. The effluent water had consistently lower concentrations of Fe than the corresponding mine water.

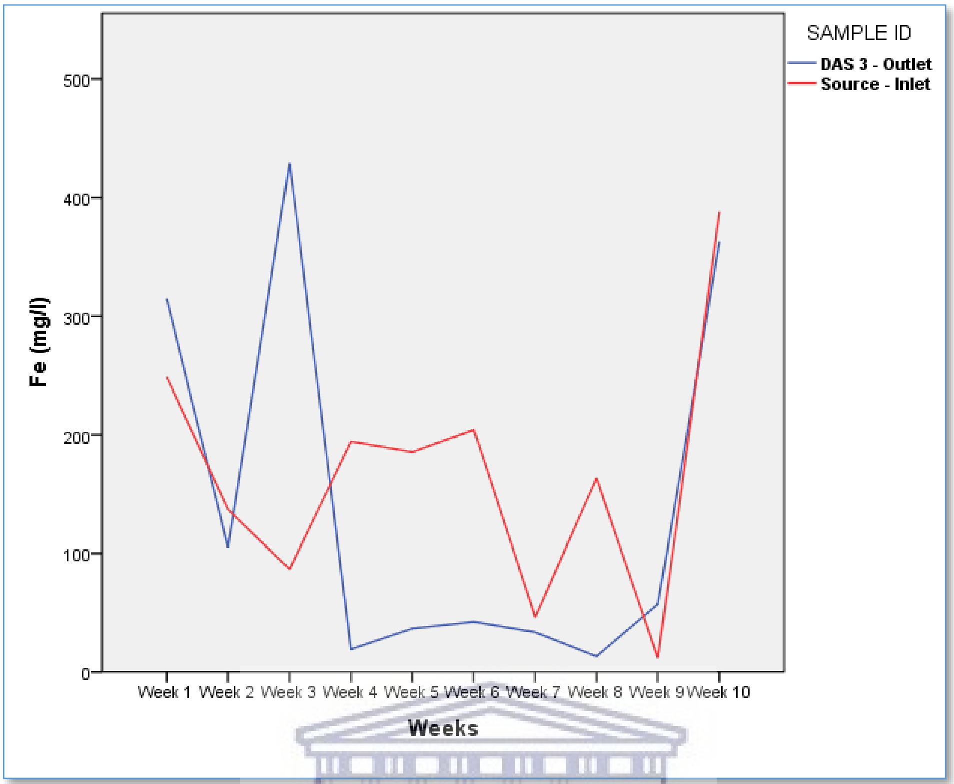


Figure 33: Comparison of the source and effluent Fe concentrations.

4.1.3.2.5 Manganese (Mn)

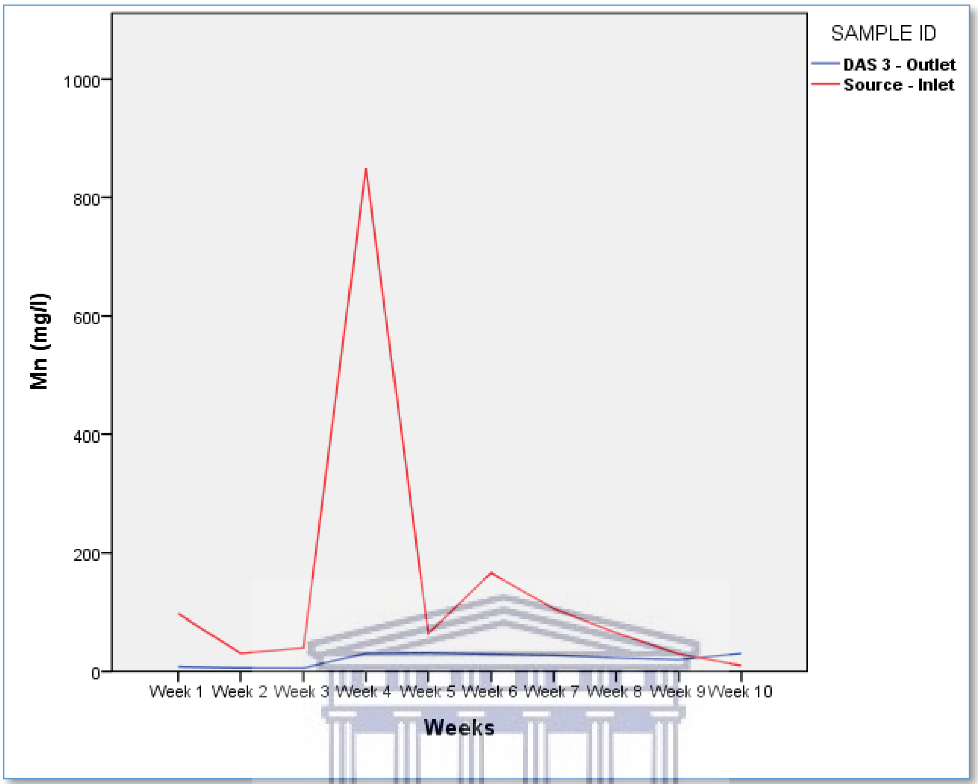


Figure 34: Comparisons of the influent and effluent Mn concentrations.

Maximum Mn removal in this study was 85%. The concentration of Mn, however, remained fairly high throughout the system as favourable conditions of pH of 10.5 which necessitate the precipitation of Mn was not achieved in the system. According to SAWQG (1996), Mn concentrations exceeding 20 mg/L will cause extreme aesthetic effects and chronic toxicity.

4.1.3.2.6 Sulphates (SO_4)

The steady decline in the sulphate concentration in the DAS system from week 1 to 10 (Figure 35) has an inverse correlation with the increase in pH. The decline in sulphates with the increase in pH is due to the liberation of Ca species which further enhance the consumption of sulphates through biological reactions. It was observed that after week 7, SO_4 reduction started decreasing with time and this is attributed to clogging and depletion of the treatment materials The removal efficiency of sulphates throughout the treatment plant was 59%. Sulfate reduction is important in the system for more effective secondary alkalinity addition and the removal of metals.

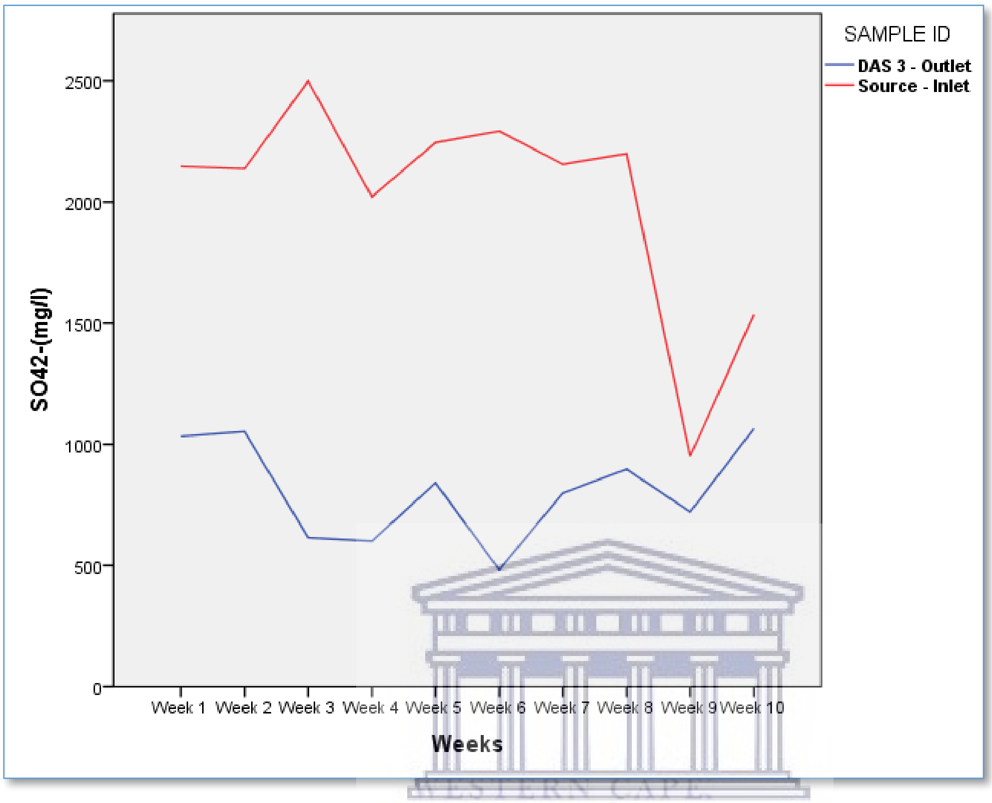


Figure 35: **Comparisons of the source and effluent SO_4^{2-} concentrations**

The removal of sulphates indicates the effectiveness of the treatment system and the increased pH which is essential in the precipitation of some toxic metals. There was substantial contaminants removal in DAS treatment systems except for Fe. The treatment plant was efficient in the removal of Pb, Cr, Cu, As, Al, Ni, Mn, Zn, and Mg.

4.2 Data distribution curves of selected variables

It is critical to ensure that the data are normalized when using multivariate statistics. This ensures that one is able to get the best results and the most reliable interpretation of multivariate analyses; thus, transforming parameters to normal distribution. The normality distribution test of the data for the following variables: pH, TDS, EC, Al, Fe, Cr, Cu, As, Pb, Ni, Mg, Ca, Zn, SO_4 and Mn under study were checked by analysing statistical values of kurtosis and skewness.

Several other tests for normality include the Shapiro-Wilk (test statistic, W) and the Kolmogorov-Smirnov (test statistic, D). The Shapiro-Wilk test statistic (W) is frequently used; it ranges from zero to one, with small p-values (less than 0.05) indicating rejection of the normality hypothesis (Grabow *et al.*, 1999). Greater than 0.05 indicates that the evidence is insufficient to reject the null hypothesis, implying that the data are indeed normal.

It was determined that EC, Al, SO_4, Mg, Ni, Ca, Zn, Cr, Mn, Cu, As, Pb and Fe concentrations do not follow a normal distribution. The coefficient of skewness is a measurement of variability. The coefficient of skewness is zero in perfectly normally distributed data. Values greater than one indicate that there is a degree of skewness that needs to be addressed (Grabow *et al.*, 1999).

The non-normal data showed that the value of skewness for Al was (5.48), Fe (0.86) and Mn (6.47), and the kurtosis values were Al (34.92), Fe (-0.63) and Mn (44.02) indicating that the data were highly positively skewed and are not normally distributed as shown in Table 15**Error! Reference source not found.**.

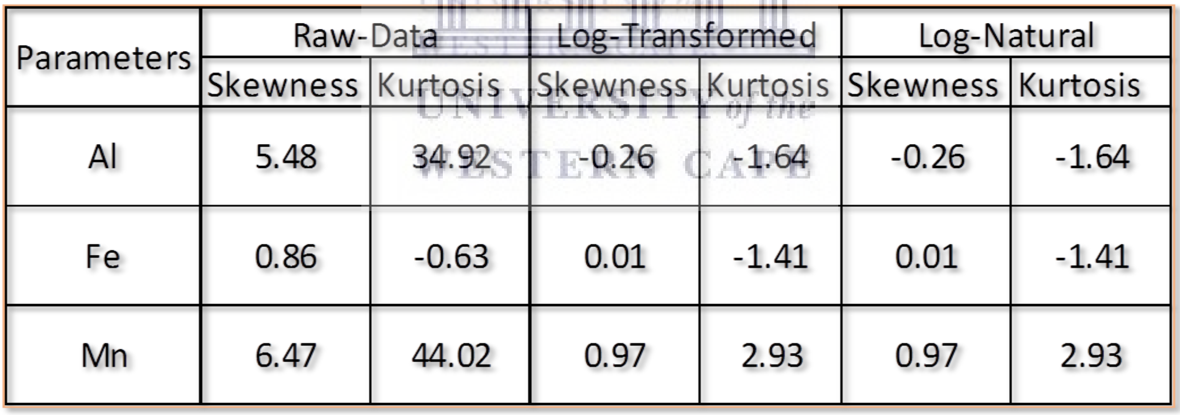
In water quality and hydrologic variables, log transformations are the most common (Gaugush, 1986). The raw data (x) for all of the parameters under consideration were log-transformed using x = log 10(x) to bring the distribution closer to normal. The log-transformed data showed some enhancements while minor changes were observed when the data were transformed using the log-normal method. After the transformation, the kurtosis improved to Al (-1.64), Fe (-1.41) and Mn (2.93), and the value for the Skewness improved to Al (-0.26), Fe (0.01) and Mn (0.97), respectively.

According to Adamu Mustapha *et al.*, (2012), log transformation works by removing outliers and normalizing geochemical and environmental data. Although the log transformation is commonly used to obtain a normal distribution, it can also be used to standardize datasets and reduce the impact of outliers and extreme cases.

Furthermore, Lettenmaier *et al.*, (1991) reported that water quality and environmental data do not always follow probability distributions such as the normal and log-normal distributions, which are the foundations of many classical statistical methods. For this study, the log-transformed data were used as the data are nearly normally distributed except for pH. The pH of the water ranges from acidic to moderately alkaline.

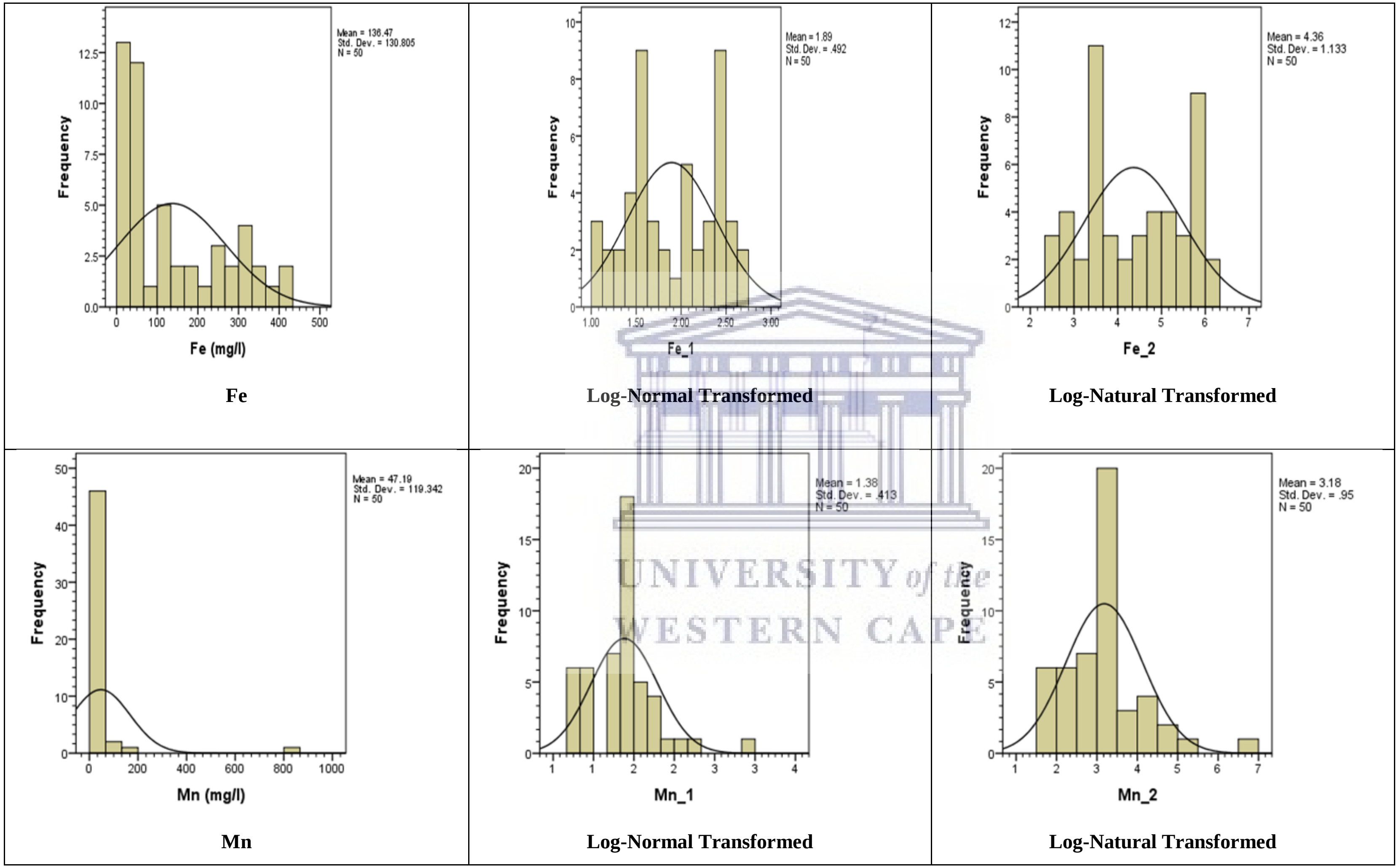
Table 15 and Figure 36 show examples of the variables in their original, log-transformed, and natural logarithm sorts. Table 11 displays the transformed data's median, mean, minimum, maximum, and standard deviation for trace elements. The mean and standard deviation values reveal significant variations in the chemical composition of the samples.

Table 15: Values of kurtosis and skewness test for normality tests for log-transformed and log-natural



Parameters	Raw-Data		Log-Transformed		Log-Natural	
	Skewness	Kurtosis	Skewness	Kurtosis	Skewness	Kurtosis
Al	5.48	34.92	-0.26	-1.64	-0.26	-1.64
Fe	0.86	-0.63	0.01	-1.41	0.01	-1.41
Mn	6.47	44.02	0.97	2.93	0.97	2.93

Note that the standard error value for Skewness is 0.337 and for kurtosis 0.662



Fe

Log-Normal Transformed

Log-Natural Transformed

Mn

Log-Normal Transformed

Log-Natural Transformed

Figure 36: Histograms showing the non-normal, log-normal and log-natural distribution of selected variables.

4.2.1 Correlation Analysis

The Pearson correlation (r) analysis quantifies the linear relationship between two variables (Mackiewicz and Ratajczak, 1993). The correlation matrix is used as the first step in factor analysis to account for the degree of mutually shared variability among individual pairs of water quality variables. The linear relationship between two variables was determined using a correlation coefficient (r). The correlation coefficient (r) quantifies and measures the strength of an element's association. In this context, the proposed null hypothesis asserts that the two variables are not related, whereas the alternative hypothesis asserts that they are related. In the case of the alternative hypothesis, a small P-value indicates that the null hypothesis is incorrect and that the variables are correlated with one another (Reimann *et al.*, 2008).

A near-perfect correlation coefficient (r) is above 0.9 with 1.00 giving a perfect correlation. A strong correlation coefficient ranges between 0.7 and 0.89; moderate correlation ranges from 0.5 to 0.69. Kura *et al.* (2013) explain that those parameters with low correlation coefficients would range from 0.3 to 0.49 as shown in Table 16 below. When r = 0.5, this is regarded as a weak correlation between variables. The negative r values indicate that there are inverse relationships between chemical parameters. The closer to a near-perfect correlation between the chemical parameters suggests a common source. The correlation matrix is classified using Guilford's rule of thumb for Pearson product-moment correlation Table 16 shows Guilford’s rule of thumb for interpreting correlation coefficients.

Table 16: Guilford's rule of thumb for interpreting correlation coefficients

R-value (correlation coefficient)	Explanation
0.0 to 0.29	Weak correlation
0.3 to 0.49	Low correlation
0.5 to 0.69	Moderate correlation
0.7 to 0.89	Strong correlation
0.9 to 1.00	Near perfect correlation

The Pearson correlation analysis was applied to all the monitoring stations to identify potential relationships (Table 17). Fifteen variables, namely EC, TDS, pH, SO4, Fe, Mn, Al, Mg, Ca, Cr, Cu, As, Pb, Ni, and Zn from the water samples were analysed for inter-relations using the bivariate correlations method with Pearson correlation coefficient using the two-tailed method. The fifteen parameters were chosen due to their consistency in occurrence in measurements across all monitoring sites. DO was not chosen for analysis due to missing sampling data.

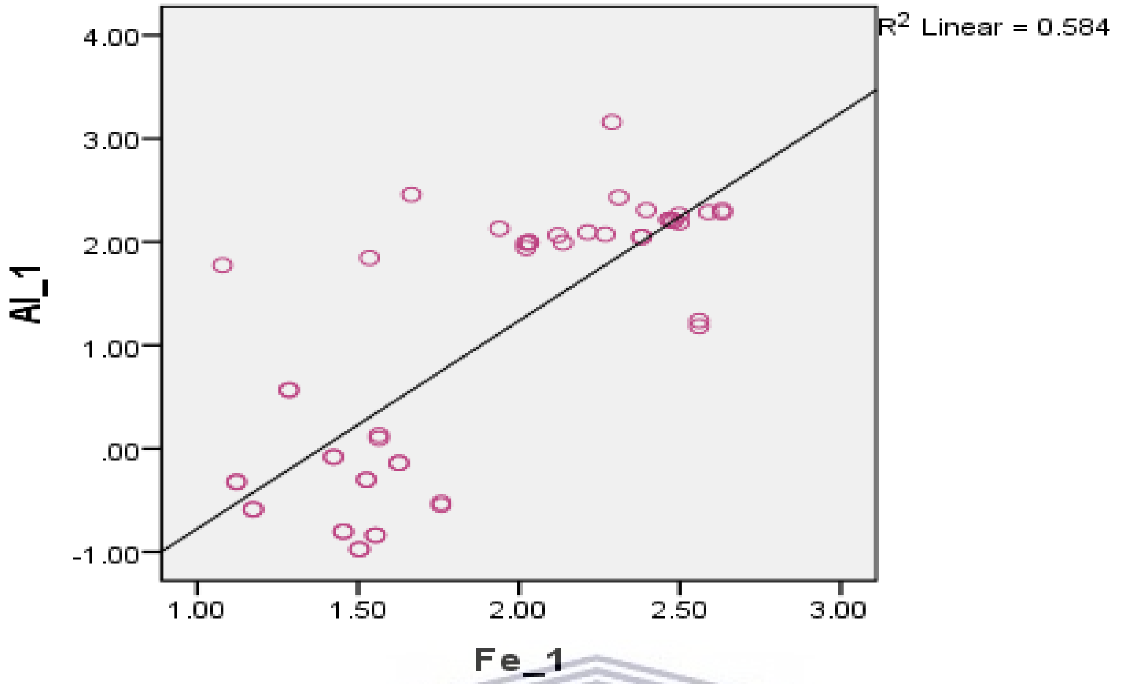
From Table 17, the results show that a strong correlation exists between Fe-Al (r = 0.764), Mg-Mn (r = 0.791) and Ni-Al (r = 0.762) indicating possibly a related source. A moderate correlation was observed between Mg- Ca, Zn-Al, SO_4-EC, EC- Mg and SO_4-TDS. Chemical and biological processes occurring in DAS 2 systems such as ion exchange could control these positive correlations. The results show that there is a low correlation between As-pH, pH-Pb, Mg-SO_4, TDS-Mn, TDS-Ni, EC-Mn, EC-Ni, EC-Zn, Al-SO_4, Mn- SO_4, Cr-Cu, Zn-TDS, Mn-EC, Mn- SO_4, and Zn-SO_4. The correlation between Mg and SO4 may point to gypsum as a source of these ions in water, but because the correlation is weak, gypsum dissolution is not the primary source. The Al-Fe relationship shows a positive linear relationship when compared to the negative relationship between Al- Ca as shown in Figure 37 below.

A negative correlation exists between TDS-As, pH-Mn, pH-TDS, pH-EC, pH-Ni, pH-SO_4, Fe-Ca, EC-Pb, Mn-Pb, Zn-Pb, Ca-Cr and SO_4-Pb. The negative correlations indicate that pH influences chemical and biological processes as well as each metal's competitive ability. The decrease in pH indicates that the variables have increased.

Table 17: Analysis for the physical and chemical determinants expressed in terms of the Pearson correlation coefficient (r)

Pearson's Correlations															
	pH	**TDS**	**EC**	**Al**	**As**	**Ca^{2+}**	**Cr**	**Cu**	**Fe**	**Pb**	**Mg^{2+}**	**Mn**	**Ni**	**SO_4^{2}**	**Zn**
pH	1														
TDS	**-.528****	1													
EC	**-.531****	**.734****	1												
Al	-.171	.239	.318*	1											
As	**.489****	**-.425****	-.239	-.059	1										
Ca^{2+}	-.207	.177	.189	**-.518****	-.144	1									
Cr	.252	-.114	-.017	.330*	.147	**-.491****	1								
Cu	-.224	.016	.166	.232	-.177	-.352*	**.457****	1							
Fe	-.072	.172	.167	**.764****	-.079	**-.455****	.212	.184	1						
Pb	**.457****	**-.585****	**-.482****	-.185	**.643****	-.117	.042	-.142	-.028	1					
Mg^{2+}	-.308*	.331*	**.518****	.157	.010	**.559****	-.248	-.130	-.067	-.258	1				
Mn	**-.443****	**.461****	**.481****	-.130	-.217	**.716****	-.262	-.088	-.262	**-.370****	**.791****	1			
Ni	**-.379****	**.448****	**.425****	**.762****	-.298*	-.302*	.327*	**.366****	**.684****	-.362*	.149	.227	1		
SO_4^{2}	**-.400****	**.589****	**.620****	**.439****	-.349*	.079	.043	.183	.247	**-.479****	**.391****	**.445****	**.603****	1	
Zn	-.185	**.391****	**.372****	**.620****	-.158	-.226	.292*	.119	.320*	**-.484****	.215	.232	**.698****	**.494****	1

NB ** Correlation is significant at the 0.01 level (2-tailed) and * Correlation is significant at the 0.05 level (2-tailed). All variables measured in mg/Land EC mS/cm and no units for pH.



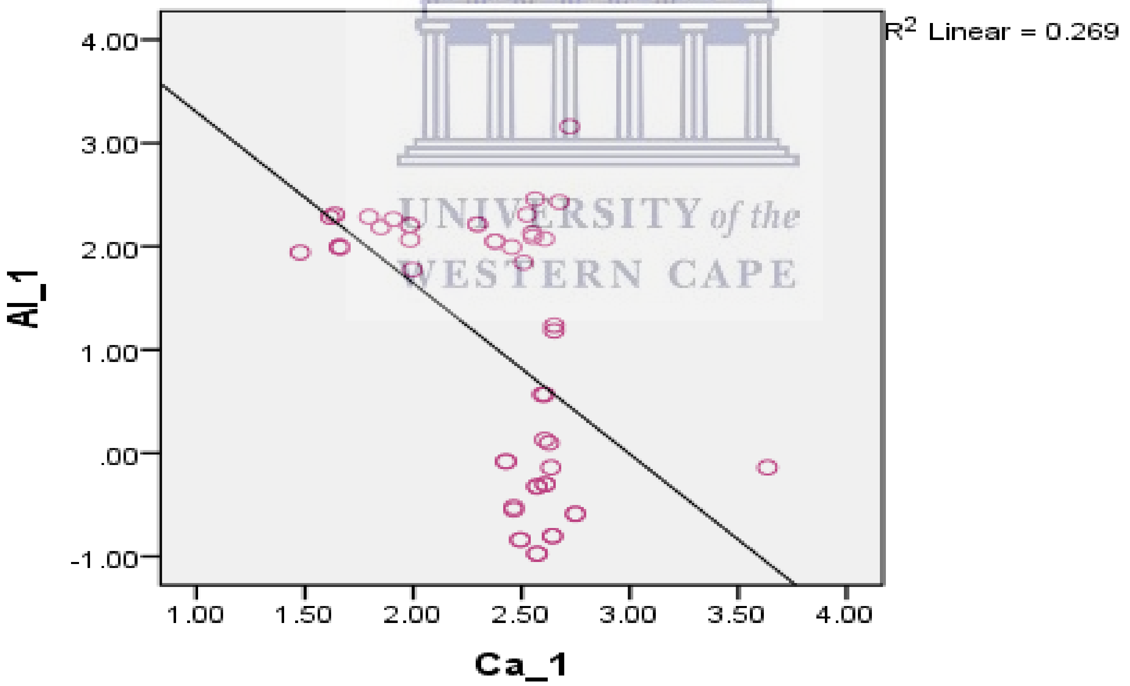


Figure 37: Scatter plots of Fe and Al and Ca and Al measured in mg/l.

4.2.2 Multivariate Statistics

Multivariate analyses were performed on the data collected in the study to determine "Potential hidden" relationships as well as controlling parameters in the DAS system using IBM's SPSS 20 software. Multivariate techniques identify and quantify multivariate patterns that emerge from the variable set's correlation structure (McGarial *et al.,* 2000). Water collected from the sampling sites was examined for the physicochemical parameters during the duration of the study. The average concentration for each parameter at the influent point was measured and compared to the effluent. Some marked variations in the parameters were observed between sampling sites, see Table 18. The data were subjected to FA in order to identify the variables responsible for the majority of the variation in water quality in the DAS system. The preferred extraction method was the principal component.

FA was used to determine the significance of various variables in the dataset (Zhang *et al.,* 2009). The total number of possible sources of variation in water quality data is reflected in the number of factors generated by a factors analysis. The first factor has the highest eigenvector sum and is the most significant source of variation in the data on water quality. Varimax rotation was used in this study to maximize the variance of loadings among factors and chemical constituents.

The final factor is the least important process that contributes to variations in water quality. The factor loadings are interpreted as the coefficients of correlation between the variables and the factors. The significance in factor analysis is determined by the eigenvalue (Mustapha and Nabegu, 2011).

Factor analysis was performed on 15 variables (EC, TDS, pH, Al, Ca, Cr, As, Cu, Pb, Fe, Mg, Mn, Ni, SO_4 and Zn of the water samples.

Table 18 shows the factors that were initially determined, their eigenvalues, and the percentage of variance contributed to each factor using the varimax rotation method with Kaiser Normalization.

Table 18: Factors loading of the DAS water quality

Total Variance Explained

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.298	35.321	35.321	5.298	35.321	35.321	3.434	22.893	22.893
2	3.566	23.771	59.091	3.566	23.771	59.091	3.203	21.354	44.247
3	1.446	9.639	68.730	1.446	9.639	68.730	3.056	20.371	64.618
4	1.105	7.368	76.098	1.105	7.368	76.098	1.722	11.480	76.098
5	.837	5.581	81.679						
6	.659	4.395	86.074						
7	.477	3.177	89.251						
8	.420	2.801	92.052						
9	.350	2.333	94.384						
10	.281	1.870	96.255						
11	.193	1.285	97.539						
12	.170	1.130	98.669						
13	.115	.764	99.433						
14	.066	.442	99.876						
15	.019	.124	100.000						

Extraction Method: Principal Component Analysis.

Four significant factors emerged from the factor analysis. These variables account for 76.098% of the total variance in data sets. Only factors with Eigenvalues 1 were considered, resulting in four significant factors that explained 76.098% of the cumulative variance in the data set, as shown in Table 18. The following factors were indicated considering the general hydrochemical characteristic of the water in the study area:

- Factor 1: Al, Fe, Ni
- Factor 2: Mn, Mg, Ca, EC and SO_4
- Factor 3: TDS
- Factor 4: Cr, Cu

The total variance explained by these four factors (factor 1, factor 2, factor 3 and factor 4) is 22.89% for factor 1, while factor 2 explains 21.35%, factor 3 explains 20.37% and factor 4 explains 11.48% respectively.

Figure 38 below shows the scree plot with eigenvalues for each component. The scree plot indicates the distinct changes in the slope from the first to the fourth component. As a function of the FA number, the eigenvalues are sorted from large to small. Factor loadings were categorized as strong, moderate, or weak based on loading values of 0.75, 0.75-0.50, and 0.50-0.30. (Al-Badaii *et al.*, 2013).

Factor loadings of the hydro-chemical parameters analysed show that Al, Fe, Ni, Zn had high positive significant loading. Factor 1 causes the most variance within the data. pH, Mn, Ca and Pb presented a negative contribution to the variation in Factor 1.

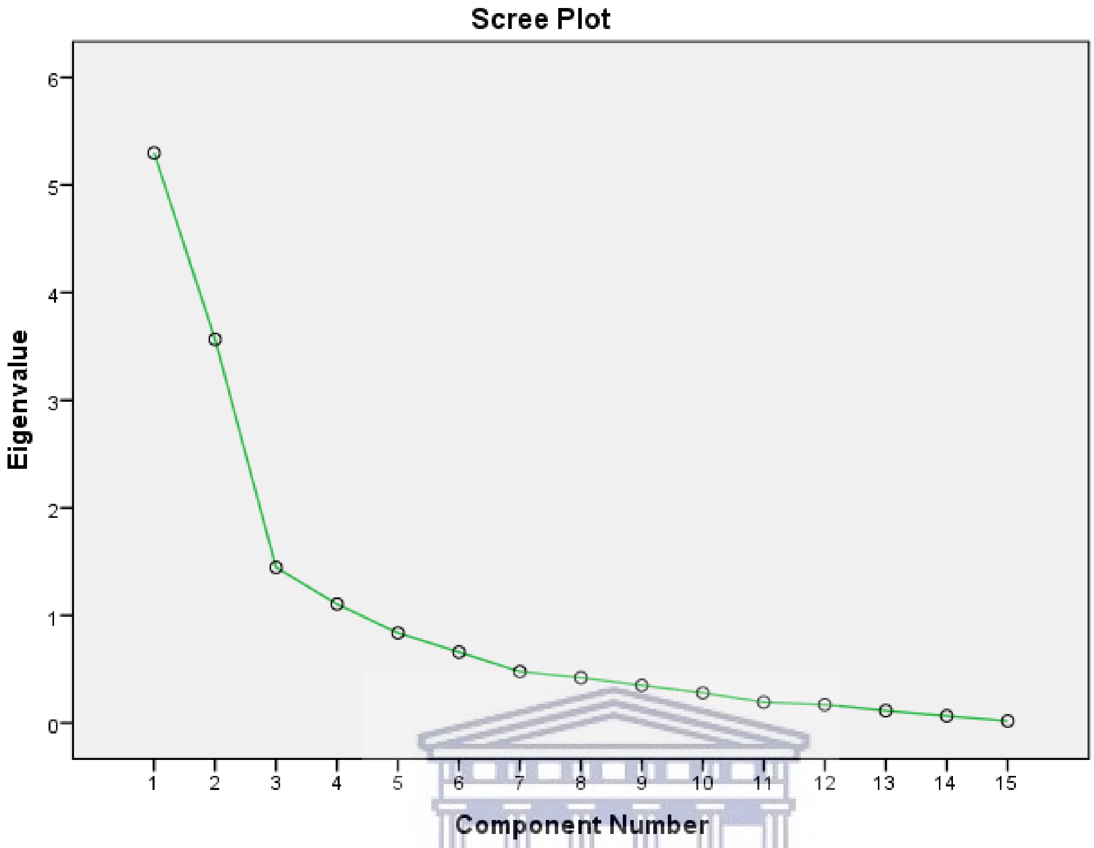


Figure 38: Scree Plot displaying the Eigen Values for each component.

Factor 1 accounts for 22.89% of the total variance with a strong significant loading of Al followed by Fe, Ni and Zn. The factor represents samples that are enriched with metalloids and related elements. This trend could indicate a related source. Acid mine drainage from coal mining areas is linked to the variables mentioned. The geochemical weathering of sulphate minerals derived from mine drainage helps to enrich the water with trace metals. There are active coal mines all around the study area. Chemical element concentrations, on the other hand, are not a direct indicator of the aforementioned potential contributors because these chemical elements can also come from natural biochemical processes. As a result, more investigations are required to determine the sources of these elements.

Table 19: Factor Analysis results with qualifying loading values above 0.5 (highlighted in red)

Rotated Component Matrix^a				
	Component			
	1	2	3	4
pH	-.093	-.328	**-.678**	.073
TDS	.285	.426	**.671**	-.030
EC	.292	**.623**	.425	.099
Mg^{2+}	.098	**.908**	.011	-.193
Al	**.941**	.048	.036	.129
Fe	**.867**	-.180	.019	-.049
Mn	-.143	**.883**	.280	-.068
Ca^{2+}	-.529	**.625**	.151	-.365
Ni	**.788**	.223	.318	.296
SO_4^{2}	.390	**.542**	.442	.187
Zn	**.671**	.267	.268	.269
Cr	.255	-.113	-.241	**.800**
Cu	.084	-.091	.185	**.817**
As	.021	.093	**-.887**	.030
Pb	-.118	-.224	**-.783**	-.095
Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization.				
a. Rotation converged in 5 iterations.				

Factor 2 of the dataset is shown to consist of EC, Mg, Mn, Ca causing high significant loadings while SO_4 shows moderate loading. As illustrated in

Table 19 with the correlation matrix, EC, Mg, Mn, Ca in the solution are positively correlated. Factor 2 accounts for 21.35% of the variance with Mg having the highest loading followed by Mn, Ca’ EC and SO_4. On the other hand, only pH shows negative loading on both factors. The results correspond to the strong negative correlation of pH with many of the variables. The moderate to high loadings of Mg and Ca could be attributed to the dissolution of carbonates in the DAS system adding alkalinity into the system. Factor 3 accounts for 20.37% of the total variance with a strong significant loading of TDS. Factor 4 accounts for 11.48% of the total variance with a strong significant loading of Cr and Cu.

In summary, the four factors represent two processes, which are:

- Pollution from coal mining upstream
- The biochemical process from the organic matter in DAS 2

According to the literature, the study area's primary land uses are mining and agriculture. According to the results of the factor analysis, pollution from coal mining areas upstream was the main determinant of water quality. When selecting a water treatment process, it is critical to consider the removal efficiency of the variables that influence the quality of the water.

4.3 The durability and capability of the DAS system in reducing trace metals and sulphate

Field monitoring and sampling of water were done regularly to assess the DAS system's performance and effectiveness in treating AMD from the abandoned mine. The treatment system showed variable performance with each cell varying in its removal efficiency of metals and metalloids. The treatment system showed positive outcomes in the first month of set-up in terms of the removal efficiency and was blocked after the second month of the experiment due to clogging. A study by Dube *et al*, (2010) recorded similar findings in their study conducted at eMalahleni on passive treatment technology. According to Dube *et al.*, (2010), the increased pH values are due to the dissolution of calcite liberated Ca which precipitate Al and Fe species which then coats the substrate of the system. Evidence of precipitation of Al^{2+} was observed on top of DAS 2 in the fourth week of operation.

The first cell achieved a significant pH shift of 3 to 5 in the decant mine water during the first month of operation. This condition was due to the dissolution of limestone generating an alkaline condition thus precipitating some potential harmful elements including As, Cr, Cu and Pb. The same results were recorded for Al, Mn, Mg and SO_4. EC was effectively reduced from the first 5 weeks of operation throughout the treatment plant.

The reduced removal performance of the system which was recorded from week 5 support findings by Dube *et al.*, (2010) that stated that the system chokes after some time due to low redox conditions. The precipitation of some chemical elements resulted in the coating of the substrate rendering it ineffective in liberating Ca species. Precipitated salts were observed along the waterways and at the bottom of each DAS system from week 5 clogging the system and cutting water movement through the system.

The concentration of Ca was observed to increase in the drainage throughout the system but alkaline conditions were not achieved. Fe concentrations dropped for the first 5 weeks and increased on the last 10th week before the system was vandalised. The overall removal efficiency of the Fe species was low at 15% due to the presence of high concentration of Mn species. Both species compete for oxygen in the system for oxidation. The decline in the effectiveness of the DAS system to liberate Ca^{2+} after week six weeks saw a significant decrease in the precipitation of Fe.

Sulphate concentrations were reduced for the first 5 weeks due to additional alkalinity generation influenced by biological reactions generated through the microbial sulphate reduction process. The SO_4 level in the influent averaged 1154 mg/L which substantially decreased in the DAS 2 and DAS 3 cells to an average of 820 mg/L. This hypothesis is supported by the fact that when the influent and effluent water quality were compared, average sulphate concentrations decreased by 59%.

4.4 Applicability of passive treatment

The applicability of passive treatment technologies is dependent on the geochemistry and mineralogical characteristics of the decanting mine water and environmental conditions and geomorphology of the area. The Witbank Coalfields are best suited for various technologies of both passive and active.

Anoxic limestone drains (ALDs), open limestone drains (OLDs), anaerobic wetlands (ANWs), Reducing Alkalinity Producing Systems (RAPS), and Sulphate Reducing Bioreactors are all potential passive treatment systems for net acidic water (SRB). Because the acidic mine drainage in the Witbank coalfield has high concentrations of Fe, SO_4, Al, and dissolved oxygen, ALDs may not be suitable due to possible clogging/armouring of limestone with oxides or gypsum, reducing the rate of limestone dissolution or plugging the system. In either case, the ALDs' ability to generate alkalinity could be significantly reduced, and the system could fail. Anaerobic wetlands, on the other hand, must have a long retention time and thus require a large surface area. However, all identified mine water sites have low flow rates and hence their applicability may be possible.

Nonetheless, DAS has the potential to be used to treat acidic mine drainage in South Africa's coalfields. They are thought to be suitable for treating net acidic water, even if it contains high metal and dissolved oxygen concentrations (Rötting *et al.*, 2008a). Open limestone drains have the potential to be used as pre-treatment systems in net acidic water. According to a study by Ziemkiewicz et al. (1994), open limestone channels/drains can be very useful in raising the pH and removing metals before the water enters the constructed wetlands or RAPS.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The primary objectives of the research project were to undertake hydrogeochemical analyses of the input mine water (influent) and output (effluent) within the treatment system and to measure the performance and capability of the DAS system in reducing trace metals and sulphate. While the research literature generally supports the applicability and functionality of these systems, there is a general failure to emphasize their limitations or the fact that they are biological systems with finite capacity for wastewater treatment. Water quality monitoring, assessment, and evaluation are important for pollution mitigation, control, and water resource management. Water quality assessment is critical for identifying the major role players and contributors to spatial and temporal variations in quality, which can be beneficial with regards to integrated water resource management (Wu *et al.*, 2017).

A pilot DAS system for the treatment of acid mine drainage water from a derelict mine in Witbank, Mpumalanga province was developed and built. The system was operational for ten weeks before it was vandalized. During the DAS's 10-week monitoring period, the system demonstrated promising treatment efficiencies for mine water discharge with low pH, elevated trace metals, and EC. This study focused on the performance of DAS system, and aimed to contribute to knowledge on South African DAS performance in general. This was accomplished by taking into account the percentage change in pollutants from the influent to the effluent point, as well as comparing effluent concentrations to effluent discharge standards.

Furthermore, the research goal was to shift the focus of the study to an analysis of the performance of CW systems in situ rather than laboratory-based studies where certain variables are contained or controlled.

The findings suggest that the technology can be used as a low-cost, measure to protect locally affected surface and groundwater resources, particularly in isolated and/or rural communities, while a permanent long-term solution is investigated. The DAS system successfully reduced a significant amount of potentially toxic metals in the treated water while also improving the pH. However, the system had limited success in reducing the Fe concentration, as the removal efficiency was only 15%. This could be due to the presence of Mn in the oxidation pond and cascading trench, which compete for oxygen consumption.

The average removal of sulphate in the system was only 59%. The descriptive statistics show that the mean sulphate concentration measured during the monitoring period at the influent was 2019 mg/Land 810 mg/L at the effluent. Bivariate statistics of the measured sulphate concentrations with the pH values show that they are inversely correlated.

Al, As, Ca, Cr, Cu, Mg, Mn, Ni, Pb, and Zn are present at the decant point as a result of mineral leaching (particularly silicates, oxides, and sulphates) associated with the coal layers and host rocks (sandstones, siltstones, shales and limestone’s).

The study's findings indicated that the DAS system performed inconsistently, except for Al (84%), Ni (84%), Zn (73%), and Mn (85%) removal.

With the help of factor analysis, the hydro-chemical data was reduced to four factors, which account for 76.098% of the total variance in the dataset. Water composition control processes were found to be the most significant contributor to data variance, while Factor 4 was found to be the least significant contributor to data variance.

A sample with a high concentration of metalloids and related elements is represented by Factor 1. This pattern may be indicative of a related source of information. There is a connection between the variables listed above and acid mine drainage from coal mining areas. The geochemical weathering of sulphate minerals derived from mine drainage contributes to the enrichment of trace metals in the water's composition.

The study area is surrounded by coal mines that are currently in operation. Because these chemical elements can be obtained naturally through biogeochemical processes, the concentrations of the aforementioned chemical elements are not always indicative of the presence of the aforementioned potential contributors. The origins of these elements must therefore be investigated further to determine their origins. This study established that factor analysis is a valuable technique for assisting decision-makers in determining the extent of pollution using practical pollution indicators. It could also serve as a rough guideline for prioritizing potential preventative measures in the basin's proper management of its surface water resources (Boyacioglu *et al.*, 2004).

Furthermore, some of the chemical determinants were compliant with one or more of the guidelines as shown in Table 14. However, Fe, Mn, SO_4 and Al were non-compliant with the SAWQG (1996) domestic water use threshold.

From these findings, a conclusion can be drawn that passive treatment plants are effective in treating AMD as a short-term solution.

5.2 Recommendations

DAS behave as natural systems and thus require a better understanding if they are to operate effectively. It is recommended that future work on the DAS performance in South Africa include monitoring over a longer period. The main limitation of the study could be retention time maintained for the DAS system, which is up to 24 hours, which might be insufficient to allow for metal removal through precipitation and other removal mechanisms. Furthermore, flow rates should be monitored more closely because obtaining flow rate data over a two-week period did not provide information about perturbations in the flow caused by peaks occurring at specific times of the day.

Future research on DAS performance in South Africa should include monitoring for a longer time, e.g. one year, to capture performance during both cooler and warmer months. Additionally, flow rates should be monitored more closely, as obtaining data over two weeks did not reveal any perturbations in the flow caused by daytime peaks. Additional units for Fe removal are required.

Improved performance of the DAS systems can be achieved by improving system management, operation, and maintenance, as well as system design. Increasing the retention time for design purposes, as a long retention time is an important factor in contaminant removal; the retention time can be increased by increasing the volume of the system.

Armouring is a significant constraint on the use of limestone in DAS. As previously stated, when alkalinity is added to AMD in the presence of oxygen, iron oxyhydroxide precipitates to form. These precipitates can form on the surface of limestone or other alkaline-contributing media, forming a barrier that can slow or stop further alkaline-contributing substrate dissolution.

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APPENDIX 1- HYDROCHEMICAL DATA

Project	Phase20	**Client**	Boitumelo
Job		**Order No.**	
Date		**Method**	ICP-MS & IC

Item		**Price**	**Cost**
Total			**R 0.00**
TM-CHE010 IC analysis	1		R 0.00
TM-CHE003 ICP-MS Quants	1		R 0.00

	pH	**TDS (mg/l)**	**TEMP (^{o}C)**	**EC (uS/cm)**	**Mg (mg/l)**	**Al (mg/l)**	**Ca (mg/l)**	**Fe (mg/l)**	**Mn (mg/l)**	**Ni (mg/l)**	**Zn (mg/l)**	**Cr (mg/l)**	**Cu (mg/l)**	**As (mg/l)**	**Pb (mg/l)**	**SO42-(mg/l)**
Source	2.7	3968	22	4566	204.24	203.15	334.56	248.94	97.38	2.34	7.26	21	86	<4	< 6	2147.57
	2.81	2760	36.2	4092	145.85	98.5	284.8	137.1	30.13	1.68	6.13	54	92	141	8	2138.2
	2.63	3270	27.2	5032	176.83	134.27	354.21	86.95	39.27	2.08	6.83	21	143	10	6	2499.55
	2.63	3239	12.7	1975	1286.75	1444.59	526.42	194.49	849.8	20.04	58.23	24	68	<4	6	2021.96
	2.49	3878	26	5967	201.39	118.24	403.24	185.56	63.71	2.11	8.06	50.55	98.06	149.78	9.51	2246.02
	2.73	5091	23.5	7832	338.55	269.4	472.35	204.32	166.27	3.47	10.17	54.41	165.55	161.77	8.92	2293.34
	2.6	3612	19	5558	235.74	287.09	365.23	46.29	105.68	3.1	9.48	51.33	144.17	151.37	8.76	2155.94
	2.95	3424	20	5268	191.72	123.83	356.87	163.45	65.08	1.94	5.3	49	169	112	20	2199.71
	2.5	1401	22	2156	66.94	59.44	99.2	11.99	28.92	0.7	1.79	62	98	51	20	951.36
	2.8	1470	23.5	2256	38.566	193.413	62.406	388.284	9.445	1.601	3.712	54	166	162	9	1536.26
Pre-Treatment	3.5	2968	25.4	2190	20.689	98.949	45.66	107.414	5.958	0.86	2.308	20	104	10	20	1582.73
	3.5	2660	27.1	1485	49.456	0.258	559.423	14.926	56.827	0.675	1.284	54	92	41	8	553.22
	3	3270	22.3	2140	19.631	0.828	267.534	26.522	25.278	0.481	8.808	20.0	92.0	48.0	8.0	1128.68
	2.7	1283	24.2	2170	30.039	0.157	438.78	28.455	42.547	0.495	0.999	24.0	44.0	19.0	8.0	985.27
	3	3278	23.4	3080	24.239	0.145	311.173	35.847	27.419	0.489	1.047	32.0	92.0	20.0	<6	741.97
	2.7	3091	25.3	3240	26.129	0.106	373.012	31.919	32.079	0.501	0.916	28.4	126.0	17.1	< 6	898.14
	3.5	3910	19.6	3220	30.439	111.884	238.215	240.331	16.659	1.212	2.457	36.5	106.9	73.2	8.2	1607.4
	3	3424	23.5	2290	29.921	160.091	96.326	302.049	9.134	1.283	3.235	32.6	92.5	48.1	6.0	1956.77
	3	1411	22.5	1485	32.928	163.665	197.78	292.431	14.937	1.334	2.618	32.9	76.0	50.6	6.3	687.08
	3.5	1470	23.1	2010	32.88	69.968	322.643	34.351	17.825	0.613	0.911	41.1	136.4	78.8	< 6	1402.99
DAS 1	6	2468	25.4	1990	29.921	160.091	96.326	302.049	9.134	1.283	3.235	20.0	82.0	<4	<6	1956.77
	6	2260	27.1	1970	20.689	98.949	45.66	107.414	5.958	0.86	2.308	24.0	89.0	<4	<6	553.22
	6.5	2270	22.3	1985	32.586	115.956	96.851	132.17	9.808	1.075	3.084	28.0	126.0	<4	<6	1448.98
	6.5	1583	24.2	1965	49.456	0.258	559.423	14.926	56.827	0.675	1.284	28.0	118.0	<4	<6	1582.73
	6	2278	23.4	1970	19.631	0.828	267.534	26.522	25.278	0.481	8.808	21.0	116.0	<4	<6	1128.68
	5.5	3091	25.3	2025	26.129	0.106	373.012	31.919	32.079	0.501	0.916	14.3	96.7	9.1	< 6	898.14
	5.5	2600	19.6	2030	30.439	111.884	238.215	240.331	16.659	1.212	2.457	16.8	32.5	8.8	< 6	1607.4
	5	1187	23.5	2110	30.039	0.157	438.78	28.455	42.547	0.495	0.999	21.4	156.6	9.1	< 6	985.27
	4.5	2390	22.5	1497	24.239	0.145	311.173	35.847	27.419	0.489	1.047	22.4	125.3	8.6	< 6	741.97

	3.06	2180	23.1	2180	32.928	163.665	197.78	292.431	14.937	1.334	2.618	24.7	66.6	8.2	< 6	687.08
DAS 2	6	1057	25.4	1920	34.192	183.22	80.83	314.998	7.974	1.375	3.955	19.0	79.0	<4	<6	1033.15
	6	1056	27.1	1918	21.647	97.45	46.021	105.202	6.057	0.861	2.275	22.0	89.0	<4	<6	1052.84
	6.5	1060	22.3	1925	27.633	202.961	43.495	429.014	5.775	1.452	3.485	20.0	112.0	<4	<6	614.39
	6.5	1080	24.2	1930	107.896	3.686	393.422	19.3	29.85	0.177	16.518	9.1	98.6	<4	<6	1009.53
	6	1114	23.4	2020	113.078	1.251	423.052	36.727	30.945	0.211	1	9.0	56.0	<4	<6	841.47
	6	1120	25.3	2025	119.738	0.726	431.621	42.325	28.42	0.149	0.344	5.6	14.3	7.3	<6	482.34
	6	2040	19.6	2019	103.309	0.499	406.147	33.588	26.695	0.117	0.278	4.0	13.9	7.5	< 6	798.99
	6	1924	23.5	1918	109.113	0.472	372.571	13.253	22.306	0.053	0.147	6.6	13.0	7.9	< 6	898
	5	1025	22.5	2050	50.513	0.283	290.506	57.281	19.373	0.248	0.081	2.7	12.9	7.4	< 6	720.99
	5	2013	23.1	1578	79.126	17.239	446.648	363.135	29.936	0.951	0.386	< 1	13.0	6.8	< 6	1065.41
DAS 3	6	1470	25.4	1485	24.192	153.22	70.83	314.998	7.974	1.375	3.955	16.0	60.0	4.0	< 6	1033.15
	6	1946	27.1	1940	19.647	87.45	30.021	105.202	6.057	0.861	2.275	< 1	51.0	<4	< 6	1052.84
	6.5	1496	22.3	1497	15.633	192.961	41.497	429.014	5.775	1.452	3.485	< 1	96.0	<4	< 6	614.39
	6.5	2110	24.2	2012	127.896	3.686	403.442	19.3	29.85	0.177	16.518	< 1	72.6	<4	< 6	600
	5	1910	23.4	1917	113.078	1.351	403.052	36.727	30.945	0.211	NaN	< 1	39.5	<4	< 6	841.47
	5	1576	25.3	1578	119.738	0.726	4311.721	42.325	28.42	0.149	0.344	< 1	14.3	7.0	< 6	482.34
	4.5	2035	19.6	1940	103.309	0.5	406.147	33.588	26.695	0.117	0.278	< 1	14.1	6.9	< 6	798.99
	4.5	2120	23.5	2110	89.113	0.48	372.571	13.253	22.306	0.053	0.147	< 1	13.7	7.1	< 6	898
	4	2013	22.5	2090	50.713	0.3	290.506	57.281	19.373	0.248	0.081	< 1	15.5	7.6	< 6	720.99
	4	2039	23.1	2055	61.126	15.239	446.648	363.135	29.936	0.951	0.386	< 1	19.5	7.9	< 6	1065.41