Bioprospecting of plants species with potential to uptake inorganic chemical species from gold mine tailings and acid mine drainage.

A dissertation to the University of Venda, School of Environmental Sciences, Department of Mining and Environmental Geology in fulfilment of Master's in Mining and Environmental Geology.

By

Makhado Khumbelo Priscilla (14013723)

Supervisor: Prof Gitari M.W (University of Venda)

Co-supervisor: Dr Mudzielwana R (University of Venda).

Co-supervisor: Mrs Dube G (Council of Geoscience).

October 2021

DECLARATION

I, Khumbelo Priscilla Makhado (Student No:14013723), hereby declare that this dissertation titled “Bio-prospecting of plant species with potential to uptake inorganic chemical species from gold mine tailings and acid mine drainage” submitted for fulfilment of Master’s degree in Mining and Environmental Geology at the University of Venda is my own work in design and execution and has never been submitted for any degree or examination in any other University and that all sources of information herein have been appropriately acknowledged by means of comprehensive list of references.

……………………………….. ……..11/10/2021……….

Student’s Signature Date

ACKNOWLEDGEMENTS

I would like to extend my sincere gratitude to Sasol University Collaboration Programme for funding this project.

Following Institutions for collaboration work and the people that we worked together that led to achieving most of the objectives:

My supervisors Prof Gitari M.W, Dr Mudzielwana R. and Mrs Dube G.M, and my mentor Dr Izevbekhai for the supervision, support and advice.

Crown Gold Mine for permission and assistance in collection of mine tailings, plants and leachates.

I would like to also extend my sincere gratitude to Dr Magwede K. for his assistance in plants identification.

To my colleagues Mr Shumba A., Mr Thobakgale R, Ms Mashau A., Mr Pindihama G. for assistance with field work and good suggestions for my study.

To the Enviren group for suggestions, positive and constructive critics throughout my studies.

I would like to thank my mother for the support, encouragement, all her prayers and her positivity that kept me going.

Lastly but not least I would like to thank God for giving me the gift of life and great opportunities to learn and grow every day.

ACADEMIC OUTPUT

Conference Output

Makhado K.P., Gitari M.W., Mudzielwana R., Izevbekhai O.U., Thobakgale R., Shumba, A., Dube G.M., 2020. Characterization of acidic water from decanting coal mine shafts in eMalahleni, Mpumalanga and inorganic contaminants retention capabilities by plants and sediments in surrounding wetlands. Presented in: *Mine Impacted Water: From waste to resource*, The Southern African Institute of Mining and Mettallurgy (SAIMM), Johannesburg, South Africa, virtual presentation (oral). 10-26 November 2020.

Makhado K.P., Gitari M.W., Mudzielwana R., Izevbekhai O.U., Thobakgale R., Shumba, A., Dube G.M., 2021. Physicochemical properties of Acid Mine Drainage Water from decant points in eMalahleni Mpumalanga, and contaminants retention potential of selected plants and sediments in wetlands. In: 14th International Mine Water Association Congress. 12-16 July 2021.

Manuscript in peer reviewed Journals (Under preparation)

Makhado K.P., Gitari M.W., Mudzielwana R., Izevbekhai O.U., Thobakgale R., Shumba, A., Dube G.M., 2021. Physicochemical properties of Acid Mine Drainage Water from decant points in eMalahleni Mpumalanga, and contaminants retention potential of selected plants and sediments in wetlands. *Journal of International Mine Water Association*.

Abstract

In South Africa, mining of gold and coal has huge negative impacts on the environment. This is due to the exposure of sulphide-bearing minerals such as pyrite (FeS_2) to oxygenated water during and after the extraction of ore deposits which results in the formation of acid mine drainage (AMD). Acid mine drainage is characterised by low pH ranging between 1-4, high concentration of sulphate and chemical species which degrade the water quality and threaten the life of terrestrial and aquatic organisms. This study aims at bio-prospecting plant species with potential use in phytoremediation of AMD and gold mine tailings. First batch of samples of plants, water leachates and mine tailings were collected from Crown Mine within Witwatersrand gold fields in Johannesburg, South Africa while the second batch of samples of plants, water and sediments were collected from the mine water discharging points and within the AMD impacted wetlands streams in eMalahleni, Mpumalanga Coal Fields. In the first part of the study deals with the characterization of gold mine tailings and acidic mine leachates collected from crown mines in Johannesburg and further identification of plants species with potential for use phytoextraction of inorganic chemical species from the acidic leachates and gold mine tailings. The physicochemical parameters of leachates such as pH, electrical conductivity (EC), redox potential (Eh), total dissolved solids (TDS), dissolved oxygen (DO) and salinity were measured in the field using pH multi-meter. Elemental composition of mine tailings were analysed x-ray fluorescence (XRF) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) techniques. Leachates samples were analysed for metals contents using Inductively Coupled Plasma Spectrometry (ICP-MS) and anions using Ion Chromatography. Plant samples were digested using aqua-regia method and analysed with ICP-MS for elemental composition. The results showed that the mine tailings are mainly composed of SiO_2, Al_2O_3, Fe_2O_3, MgO and K_2O as major oxides and Cr, Co, Cu, Ni, Zn, Tb, Ta, Tm, Mo, Eu, Lu, Ho and Cs as trace elements. The pH, EC, TDS of the leachates were found to be ranging from 3.31 to 5.21, 3 857 to 5 517 mS/cm and 1930 to 2704 mg/L, respectively. The leachate samples were characterized by higher concentrations of Mn, As, Cr, Al, Pb, Ca, Na, K and Fe. The most dominating anions within the leachates were Cl^- (135.97-201.28 mg/L) and SO_4^{2-} (59.39-62.65 mg/L). *Cortaderia selloana* and *Populus alba* accumulated high concentration of Mn, Zn, P, Mg, K and B in their leaves than other parts of the plant. Translocation factor (TF) reflected that *Cortaderia selloana*

plant species has the potential to translocate all the chemical species from the roots to the shoots except Se. *Cortaderia selloana* showed bioconcentration factor greater than 1 for chemical species such as B, Mn, Zn, Sr, Ca, Mg, P, and Si. Similarly, *Populus alba* showed the bioconcentration greater than 1 for Mn, Ni, Cu, Sb, Na and Mg. In addition, *Populus alba* showed bioconcentration factor greater than 10 showing hyperaccumulation ability for species such as B, Co, Zn, Ca, Cd, K, P and Sr. These plants can be used for the phytoremediation of mine tailings. Second part of the thesis focused on characterising mine water discharging from abandoned mine shafts and assessing the change in water quality from the discharging point, within retention ponds, upstream to downstream of the wetland. Furthermore, evaluating the role of sediments and native plants species in the remediation of acid mine drainage. The physicochemical characteristics such as pH, EC, TDS, Eh, DO and Salinity were found to be ranging from 2.53 to 3.6, 1066 to 2285 µS/cm, 610 to 5230 mg/L, 194 to 256.8 mV, 2.94 to 8.24 mg/L and 0.82 to 6.09 psu, respectively. The concentration of SO_4^{2-}, Cl^-, NO_3^{2-} and F^- were found to be ranging from 992.90 to 12580.38, 19.63 to 160.61, 1.77 to 23.56, and 4.76 to 14.95 mg/L, respectively. The dominant inorganic chemical species in water were found to be Ca, K, Mg, Na, Si, Al, Fe, Zn and Mn. The sediments collected along the streams showed higher concentration of Fe, Ca, Al, K, Mg, Na, P, Si, Zn, Mn, and V as compared to concentration in water. This implied that sediments are adsorbing chemical species from acid mine drainage and hence improve the quality of water. The concentration of metals in plants tissues are in the following order: Fe > Mg > Al > Mn > Zn > Cr > Ni > Cu > Co > Pb > As > Cd. Amongst all the native plant species, *Cyperus esculentus* had higher translocation factor (greater than 1) in Cr, Mn, Ni, Zn, Ca, K, Mg, Na, P and higher bioconcentration factor (greater that 1) in Cr, Co, Ni, Cu, and Zn, and a bioconcentration factor of greater than 10 in Cd, Ca, K, Mg, Na and P. This implied that *Cyperus esculentus* have the potential in phytostabilization of Cr, Co, Ni, Cu, Zn, and Cd, and Cd, Ca, K, Mg, Na and P and phytoextraction of Cd, Ca, K, Mg, Na and P. In nutshell, the results from this study showed all the plants species identified in this study (*Cortaderia selloana, Populus alba, Cyperus esculentus, Phragmites mauritianus, Cynodon dactylon, Typha capensis* and *Juncus effussus* and *Juncus lomatophyllus*) has potential for use in the phytoextraction of inorganic contaminants from the AMD and gold mine tailings. Therefore, the study recommends detailed studies optimizing the species application in phytoremediation of AMD and gold mine tailings in a pilot scale project.

Keywords: *Acid Mine Drainage, mine tailings, wetlands, native plant species, gold and coal mines.*

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ACRONYMS

AMD Acid Mine Drainage

As Arsenic

Ca calcium

Co Chromium

Cu Copper

DMR Department of Mineral Resources

DO Dissolved Oxygen

DWAF Department of Water and forestry

EC Electrical Conductivity

Eh Redox potential

Fe Iron

IC Ion Chromatography

ICP-MS Inductively Coupled Plasma Mass Spectrometry

LA-ICP-MS Laser Ablation Inductively Coupled Mass Spectrometry

MMSD Mining, Minerals and Sustainable Development

Ni Nickel

SA South Africa

TDS Total Dissolved solids

XRF X-ray Fluorescence

Chapter 1: Introduction

1.1 Background

Acid mine drainage (AMD) is one of the major environmental problems that begins when sulphide-bearing minerals such as pyrite, chalcopyrite and bornite, are exposed to oxygen and water (Jennings *et al.*, 2008; Ramla and Sheridan, 2014). The common sulphide-bearing mineral, pyrite, undergoes oxidation in a two-stage process. The first stage, producing sulphuric acid and ferrous sulphate and the second producing orange-red ferric hydroxide and more sulphuric acid (McCarthy, 2011). These processes are expressed by Eq. 1.1 and 1.2.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \qquad (1.1)$$

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 \downarrow + 8H_2SO_4 \qquad (1.2)$$

The formation of AMD in a mining environment is dependent on several factors and site conditions. These includes factors such as pH, temperature, oxygen content, chemical activity of Fe^{3+}, surface area of exposed metal sulphides, degree of saturation with water and bacterial activity (Akcil and Koldas, 2006). In South Africa AMD cases have been reported in historically gold and coal mining regions of Witwatersrand goldfields which is divided into the western, central and eastern basin, and Mpumalanga and KwaZulu Natal coal fields (Ramla and Sheridan, 2014).

Acid mine drainage is mainly composed of the chemical species that are originally from the ore and its host rock. Acid mine water discharging from abandoned flooded mines and leachates from the mine tailings cause the deterioration of the quality of the receiving water body. Acid mine drainage is characterised by low pH, high concentration of dissolved metals, metaloids and sulphates (Gaikwad *et al*., 2008). An array of scientific studies has documented the devastating impacts of AMD to terrestrial and aquatic organisms due to its acidic nature leaching potentially toxic chemical species (McCarthy, 2010; Durand, 2012; Gitari *et al.*, 2013; Odoh *et al.*, 2019). The presence and exposure of excess aluminium (Al) in acidic water results in acute respiratory dysfunction and mortality (Krewski *et al.*, 2007), whereas uranium (U) causes leukaemia (Řeřicha *et al*., 2006).

Wetlands are well known to be efficient at sequestering pollutants from contaminated water thus they serve as passive systems for water treatment (Smith, 1997; Ambani and Annegarn, 2013; Humphries *et al.*, 2017). A wetland system consists of plants, sediments, and aquatic organisms that are responsible for the adsorption, filtration, cation exchange and reduction of all chemical species (Javed *et al.*, 2019). A study by Atibu *et al.* (2018) revealed that plants and sediments play a major role in extracting pollutants. Their findings further showed that sediments have extremely high concentration of chemical species compared to the plant species. Geochemical processes or treatment mechanisms that occurs in a wetland involves oxyhydroxysulphate precipitation which results in the decrease of iron (Fe) and, precipitation of aluminium (Al) concentrations at pH less than 5 (Han *et al*., 2017). Consequently, metals like copper (Cu) and zinc (Zn) are removed with Al precipitate (Han *et al.*, 2017). Furthermore, metals are removed from the water of through adsorption and co-precipitation processes on sediments (Han *et al*., 2017).

Humphries *et al.* (2017) assessed the decrease of pollutants from AMD by a natural wetland on Witwatersrand basin by analysing the concentration of metals in water and sediments samples collected from upstream, midstream to downstream. Their study found that the concentration of metal species Al, Fe, Pb, Ni, Zn, Co and Cu decreases from upstream to downstream in both water and sediments samples. This was attributed by geochemical processes such as adsorption and co-precipitation of metals on sediments from upstream to downstream are responsible in the reduction of metal concentration.

Currently, several researchers are focusing on development of constructed wetland systems for the use in remediation of AMD. Constructed wetlands are developed in the absence of natural wetland for the purpose of remediating toxic pollutants from the wastewater. Ramla and Sheridan (2014) conducted a study elucidating the potential in utilisation of indigenous South African grasses for acid mine drainage remediation. The study used synthetic AMD and three native species (*Zantedeschia aethopica, Hyparrhenia hirta, Setaria sphacelata*) as organic substrates. Their results showed that *Hyparrhenia hirta* grown in the presence of microbes has the better potential for use in removal of iron from AMD. Moreover, the results showed increase in pH to about 8.5. Furthermore, *Hyparrhenia hirta* and *Zantedeschia aethiopica* also showed highest removal of sulphate from the AMD solution. The latter study has showed that South African native grass species can remediate AMD.

Few studies have been conducted in South Africa to investigate the use of natural wetlands in acid mine drainage remediation and to further identify native species with better potential for use AMD remediation. Most of the studies were conducted at the laboratory scale using simulated AMD, planted with either one or two of these plant species *Phragmites australis, Typha Erchhornia, Juncus and Scirpus* (Türker *et al*., 2013; Younger and Henderson, 2014; Mabhena, 2015; Peng *et al*., 2017; Pat-Espadas *et al*., 2018). The performance capacity of all constructed wetland is limited based on the available plant species and sediments used. However, natural wetlands are equipped with all the diverse species of plants, sediments, and microbial population which plays role in uptake of inorganic chemical species.

In the present study, the gold mine tailings which generates acid mine drainage which discharges into the surrounding environment were identified in Witwatersrand basin, Johannesburg, Gauteng province. The area is surrounded by various plant species surviving in the mine tailings and also in the acidic mine leachates. To date no study has actually looked into the capabilities of these plant species in the uptake of chemical species from the mine tailings and the leachates discharging from the mine tailings. Several AMD discharging points were also identified in eMalahleni, Mpumalanga Province. In these areas, AMD discharges into the surrounding wetlands and streams and this has caused several impacts on the natural environment. This study therefore aim at bio-prospecting the plant species which are surviving either in the gold mine tailings, acidic mine leachates and wetlands impacted by AMD in order to determine their potential for use in the uptake of inorganic species from mine tailings and acid mine drainage. Samples of plants, mine tailings, sediments and water were collected and analysed for the concentration of inorganic chemical species.

1.2 Problem statement

Acid mine drainage is a major environmental problem producing sulphuric acid that mobilises elements that poses potential risks to human health and ecosystems (Simate and Ndlovu, 2014). Acidic effluents have led to the pollution of both surface and subsurface aquatic ecosystem and degrading the quality of limited available freshwater. Due to high acidity, the mobility of the chemical species in the environment increases significantly (RoyChowdhury *et al*., 2015; Skousen *et al.*, 2017). Areas that are extensively affected by AMD in South Africa is the Klip River, Grootspruit flowing into Saalboomspruit, Groot Olifants River, Olifants River Catchment and Steenkoolspruit (Yibas *et al.*, 2014).

In Witwatersrand basin, Johannesburg in Gauteng Province there are heaps of gold mine tailings which are mainly characterized by toxic inorganic chemical species (Mn, Zn, Cd, Cr, Co, Cu, Al) which causes damage to the surrounding water resources and nearby environment. Moreover, the mine tailings discharge the acidic leachates which are carriers of dissolved toxic metals that contaminate the receiving water resources (Netshiongolwe, 2018).

The eMalahleni region of Mpumalanga Province is commonly known for coal mining. However, recently there are tonnes of abandoned coal mines that are discharging mine acid mine water into the natural environment and surrounding streams and wetlands. Figure 1.1 illustrate the acid mine water discharge point and the impacted wetlands. Bell *et al.* (2001) reported that coal mining in Witbank coalfield has disturbed the natural environment due to surface subsidence from old mine workings and deterioration of water quality in the Blesboklaagte catchment. The water within the catchment has been reported to have high concentration of sulphate (1440 to 3250 mg/L), total dissolved solids (2082 to 4844 mg/L) and toxic metals, and low pH (1.8 to 3.0) as a result of AMD. Moreover, the Witbank, Loskop and Middelburg dams of the Olifants River Catchment started showing elevated levels of sulphate and total dissolved solids concentrations as early as 1970 (CER, 2016). In 2011 DWA found that mining of coal around the Wilge, Bronkhorstspruit, Klein Olifants and Olifants Rivers are the main contributors to poor water quality and in-stream and riparian habitat conditions. Over the years there have been a noticeable decline of fish population in the Loskop Dam on the Olifants River in Mpumalanga.

Figure 1.1: Disturbed land surface and discharging point of AMD in Blesboklaagte.

Owing to the environmental impacts caused by the mine tailings and acidic mine drainage observed in Witwatersrand and eMalahleni regions, focus is now to develop cheap technologies for use in phytoremediation of the impacted environments. The use of invasive plants species has proved to be problematic in remediation processes and this is due to reduction of both surface runoff and groundwater recharge, due to increase in the plant's biomass (Gorgens and Van Wilgen, 2004) The increased plant's biomass is prone to wildfires which causes damage to the natural vegetation and soil, and consequently leads to erosion. In order to eradicate the challenges of introducing invasive plants, it is better to identify native plants species that are already colonizing the contaminated area. These plants of interest should show resilience in harsh condition and be able to uptake contaminants without showing toxicity. Therefore, the focus of this study is to bio-prospect naturally growing plants species on mine tailings, mine water discharging points, wetlands, ponds and streams, and evaluate their capabilities in the uptake of inorganic chemical species.

1.3 Research objectives

1.3.1 Main objective

The main objective of this study is to bio-prospect native species surviving in gold mine tailings of Johannesburg crown mines and AMD impacted wetlands in eMalahleni, Mpumalanga with potential for use in phytoremediation of mine tailings and AMD.

1.3.2 Specific objectives

- To characterize the physicochemical properties of gold mine tailings and leachates from collected from Crown Mines, Gauteng Province.
- To identify the plant species surviving in the gold mine tailings and leachates ponds and further evaluate their inorganic chemical species retention capabilities.
- To characterize the acidic mine water discharging from the decant points into the wetland streams in eMalahleni region of Mpumalanga Province.
- To investigate the inorganic contaminants retention by sediments and further bio-prospect native plant species surviving in the wetlands with better metal retention capabilities.

1.4 Research questions

- What are the physicochemical properties of gold mine tailings and leachates from collected from Crown Mines, Gauteng Province?
- Which plant species are surviving in the Gold mine tailings and leachates ponds and which retention capabilities are responsible for the remediation of inorganic chemical species?
- What are the characteristics of acidic mine water discharging from the decant points into the wetland streams in eMalahleni region of Mpumalanga Province?
- What are the physicochemical properties of acid mine drainage, sediments and plant species from discharging point, retention ponds, streams and wetlands?
- Which inorganic contaminants are retained by sediments and which native plant species surviving in the wetlands have better metal retention capabilities?

1.5 Significance of the study

McCarthy (2011) indicated that South Africa is classified as a water-scarce country, with most regions having a negative water balance, where the amount of evapotranspiration is greater than the received precipitation. Pollution from mining activities, particularly AMD is threatening water security and aquatic biodiversity. Various active and passive treatment methods have been used to remediate AMD, with passive methods particularly the use of constructed wetlands gaining momentum (Sheridan *et al*., 2013; Ramla *et al*., 2014; Pat-Espadas *et al*., 2018). Passive treatment in SA is limited to laboratory and pilot scale systems (Par-Espasdas *et al*., 2018). The knowledge regarding the uptake mechanism of chemical species in AMD through hyperaccumulators is available, however there is still a need to acquire more information on native plant species. Thus, this study presented a paradigm shift in AMD remediation technology using natural wetlands and native plant species which are proven to be effective.

This study identified native plant species and assessed their potential for bioconcentration of chemical species along the wetlands, streams, and tailings ponds. It is important to identify native South African plants with bioconcentration potential of chemical species in AMD because they are safe to be planted in other AMD impacted water bodies. Unlike alien species, native plants have low to relatively no environmental impacts and they are able to provide habitat to organisms (Magee *et* *al*., 2019). According to Sarma (2011) identification of plants with hyperaccumulating potential of chemical species is vital because they represent remediation of metal-polluted sites. Sarma (2011) indicated that native plant species require less control and management measures as compared to alien species, and they can easily adjust to new climatic condition. The identified native South African plant species have the potential to be used in the constructed wetlands in remediation of AMD and for metal pollutants.

National research AMD policy recommended or set a target that medium to long term treatment options should be considered in remediation of AMD (Strydom *et al*., 2016). The main factors to consider while choosing the treatment options are cost-effectiveness, scattered small scale sites, amount of treated water and uses of treated water. This study has contributed to the targets in place by providing medium to long-term remediating solution of AMD at a large scale. The use of natural wetlands is therefore cost-effective since natural resources are utilised.

1.6 Thesis structure

This thesis is divided into 5 chapters, each chapter explaining different aspects of the study. Below is the summary of each chapter.

CHAPTER 1: Introduction

Gives a brief background of AMD formation and, associated problems and methods that have been used to treat this problem. An outline of the objectives, research questions and significance of the study.

CHAPTER 2: Literature review

This chapter provides a detailed information on formation of AMD, physicochemical characteristics, and impacts of AMD. It covers the active and passive remediation methods of AMD, with their advantages and disadvantages. Wetlands are discussed in this section as one of the passive remediating method and performance of natural wetlands on AMD remediation. The metal accumulation efficiencies entailing bioconcentration and translocation factor of inorganic contaminant is also mentioned.

CHAPTER 3: Physicochemical Characterization of abandoned gold mine tailings, leachates, and potential of *Cortaderia selloana and Populus alba* for phytoextraction of inorganic contaminants.

This chapter gives a brief explanation of Witwatersrand gold mineralisation, mine tailings and the leachates from the mine tailings, and associated environmental impacts. It also looks at phytoremediation of mine tailings. This chapter further characterises the gold mine tailings, leachates and two plant species naturally growing on mine and assess the bioconcentration potential of the inorganic contaminants by the two plant species.

CHAPTER 4: Physicochemical properties of acid mine water from decant points in eMalahleni, Mpumalanga and contaminants retention potential of selected plants and sediments in wetlands.

This chapter reports on cases of contaminated water at household level, the negative environmental and health impacts of mine water. It further characterises mine water from the discharging points, streams and wetlands, sediments, and native plant species. The change in water quality from upstream to downstream of the wetlands and the role of sediments and plants in the retention of inorganic contaminants is also discussed.

CHAPTER 5: Conclusion and Recommendations

This is the last chapter, and it provides a summary of the main findings of this study and recommendations for further research.

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Chapter 2: Literature Review

2.1 Introduction

Acid mine drainage is formed when sulphide-bearing minerals (such as pyrite and chalcopyrite) react with oxygen and water. The oxidation of pyrite mineral phase releases dissolved iron and acidity into the aqueous phase. Acid mine drainage is characterised by low pH (<4.5) and high concentration of toxic chemical species. The major environmental problem associated with AMD is the degradation of terrestrial and aquatic biodiversity. This chapter presents a detailed literature review concerning mine tailings, the formation of acid mine drainage, physicochemical characteristics, environmental and socio-economic impacts, and remediation techniques in international and South African context. Furthermore, the role of wetlands as passive treatment systems will be reviewed.

2.2 Mine tailings

Metalliferous mines in South Africa have resulted in enormous volumes of mine tailings, which have been deposited in impoundments (Rosner and van Schalkwyk, 2000; Poswa and Davies, 2017). It was reported that in 1996 alone, a total volume of 377 million tons of gold mine waste was produced which was accounting for 81% of the total mine waste in South Africa (Chamber of Mines of South Africa, 2001). Furthermore, Rademeyer (2007) estimated that approximately 12,000 hectares of land were occupied by 150 mine tailings dump in Gauteng Province alone. Only a small percentage of the mine tailings can potentially be reprocessed, recycled, or utilized for backfilling in mine-out areas (Poswa and Davies, 2019; Sibanda *et al.,* 2019).

Mine tailings are mainly composed of finely crushed materials and they stacked in open-air tailing impoundments which are normally situated close to mining sites (Sibanda *et al.,* 2019). According to Redwan (2019) and Compaore *et al*. (2020) gold mine tailings are considered as one of the main mine waste products enriched with contaminants. Compaore *et al.* (2019) explained that the contaminants within the mine tailings can spreads all around the neighbouring areas and threaten the local soil, surface water and groundwater resources, as well as the terrestrial and aquatic biodiversity. These mine tailings contain large amounts of approximately 10 to 30 kilogram per tonne of sulphide minerals (pyrite, chalcopyrite) which are prone to generate acid mine drainage (AMD). Acid mine drainage is a global pollution problem and is generally reflected by high salt loads and acidification of the affected environment. In addition, AMD is often associated with significant concentrations of toxic trace elements and radionuclides. These contaminants remobilise under acidic conditions and migrate into the vadose zone and groundwater system.

2.2.1 Environmental problems of mine tailings

Uncovered mine tailings would vary in response to weathering processes and chemical reactions cannot be fully foretold, due to variation of mineral assemblages (Nyenda *et al*., 2020). The environmental impacts of these tailings in arid-semiarid areas are mostly resulted from the lack of vegetation cover and thus suffering from severe wind and water.

2.2.1.1 Water pollution

Several studies have reported the negative impacts of contaminants emanating from mine tailings in water system (Naicker *et al*., 2003; Coetzee *et al*., 2004; Tutu *et al*., 2005; Coetzee *et al*., 2007). Water leaches out potentially toxic soluble pollutants (e.g sulphide minerals, and metals) from the mine tailings into and transports them into the neighbouring water systems. High concentration of toxic metals (Cu, Pb, Zn, Mg, Cd, As, Ni) degrades the water quality and affects aquatic biodiversity and water supply. When these metals exist in concentrations exceeding permissible limits for domestic and irrigation as stipulated by DWAF of 1996, may result in environmental and health problems. The presence of these metals has been detected in the water and sediments systems downstream of the mine tailings in wetlands such as Klip River, Blesboklagte and Koekemoerspruit wetland (McCarthy and Venter, 2006).

2.2.1.2 Air pollution

Air can be polluted by means of wind erosion introducing toxic substances into the environment. Wind erosion of the surfaces of the mine tailings forms suspension of fine dust containing various toxic substances (e.g.CN, Si, Cd, Pb, As). One of the most hazardous substances is cyanide, when people are exposed to excessive amounts over a long period can cause damage to the cells and inhibit various enzymes to play their roles in the human body (CMSA, 2001). When the concentrations of these substances in the air exceeds the South African NEMA Air Quality Act No. 39 of 2004, they are considered to cause air pollution. The dust contains particles of silica which may cause respiratory problems to communities in the vicinity of the mine tailings dump. Several researchers have reported the cases of silicosis in communities living in the vicinity of the mine tailings dump, this is caused by the accumulation of silica dust in the lungs (Nelson *et al.,* 2010; Anon, 2019; Barnes *et al*., 2019; Knight *et al*., 2020)

2.2.1.3 Soil pollution

Soil pollution can occur either though water or wind erosion of mine tailings containing toxic contaminants into arable land. When the concentration of sulphates, iron, uranium, lead and other metals in the mine tailings exceeds the background concentration in the soil can be regarded as pollutants that may lead to destruction of flora and fauna within the ecosystem (Ndolo, 2013). Similarly, presence of these metals in higher concentration than the surrounding environment act as indicators of environmental pollution.

2.3 Formation of Acid mine drainage

Acid mine drainage and its adverse environmental impact mainly on water resources have been studied extensively throughout the world and has been reported to be mainly generated from the dissolution of unstable sulphide mineral (McGregor and Blowes, 2002; Romero *et al.*, 2007; Nyquist *et al.*, 2009). With reference to the common sulphide-bearing minerals, it is important to mention that the formation of AMD is generalised by three major chemical reactions, the oxidation of sulphide minerals (Eq. 2.1 and Eq. 2.2), oxidation of ferrous iron (Eq. 2.4) and hydrolysis and precipitation of ferric iron and other minerals (Eq. 2.3) (Kalin *et al*., 2006; Dold, 2010). In acidic environment Eq. 2.1 and 2.2 can be accelerated by acidophilic bacteria such as *Thiobacillus ferroxidans* (Quantrini and Johnson, 2019).

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad (2.1)$$

$$4Fe^{2+} + O_2 + 4H^+ \leftrightarrow 4Fe^{3+} + 2H_2O \quad (2.2)$$

Formation of AMD is dependent on different factors such as oxygen, water, and exposure of sulphide-bearing minerals. If oxygen is low, Eq. (2.2) will not occur until the pH reaches 8.5 (Luptakova *et al*., 2010), however, this reaction is the rate limiting step in pyrite oxidation because the conversion of Fe^{2+} to Fe^{3+} is slow at pH values below 5 under abiotic conditions (Simate and Ndlovu, 2014). At pH values between 2.3 and 3.5, ferric ion formed in Eq. (2.2) may precipitate as $Fe(OH)_3$ in Eq. (2.3)

(Espana *et al.*, 2005). This acidity (pH 2.5-3.5) leads to the dissolution of ores that occurs alongside pyrite hence the presence of other cations such as Ag, Cd, Co, Mn, Ni, Hg, Mo, Se and Zn in acid mine drainage (McCarthy, 2011).

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 \downarrow + 3H^+ \quad (2.3)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (2.4)$$

Simate and Ndlovu (2005) reported that the formation of ferric hydroxide precipitate is pH-dependent, and if pH is less than two (<2), ferric hydrolysis products like $Fe(OH)_3$ are not stable and Fe^{3+} remains in solution (Simate and Ndlovu, 2005). Furthermore, solids will form if the pH is above 3.5, but below pH 3.5 little or no solids will precipitate. In Eq. 2.4 Fe^{2+} is produced and if there is sufficient dissolved oxygen present, Eq. 2.2 and 2.3 will continue indefinitely, however in the absence of dissolved oxygen Eq. 2.4 will continue to completion and water will have high levels of ferrous iron (Bakatula *et al.*, 2012).

2.3 Physicochemical characteristics of AMD

The key characteristics of AMD include pH and EC, Eh, cations and anions (Alegbe *et al.*, 2019). The pH of AMD ranges between 1 and 4 (Simate and Ndlovu, 2005). The most common chemical species associated with AMD is As, Pb, Hg, Cd, Cr, Co, Ni, Cu and Zn. Gitari *et al.* (2008) reported on the composition of AMD, and found a significant concentration of Mn, Mg, Al, Cu, Pb, Na, Ni, Ca, pH values of approximately 2, as well as Fe levels greater than 6000 mg/L and sulphate levels higher than 2000 mg/L. Table 2.1 shows the characteristics of AMD leachates flowing from an abandoned mine in eMalahleni, Mpumalanga reported by Dube *et al.* (2019). Table 2.2 shows the change in characteristics of stream water impacted with AMD in different seasons, reported by Naicker *et al.* (2008).

Table 2.1: Mine water results and target quality range (DWAF standards) (Dube *et al.*, 2019).

Parameter	pH	EC	Cl	SO4	Ca	Al	As	Co	Fe	Mn
Concentration	2.70	2.70	0.90	1006.40	49.70	109.70	0.01	0.80	132.10	7.30
DWAF	6-9			0-200		0-0.15	0-0.01		0-0.1	0-0.05

*All concentrations are in mg/L, except for pH and EC (mS/cm).

Table 2.2: Analytical results for stream water samples impacted by AMD, collected over four seasons, (a) and (b) (Naicker *et al*., 2008).

(a)

Sample	pH	Eh mV	EC mS/cm	NO_3^- mg/L	PO_4^{3-} mg/L	SO_4^{2-} mg/L	Cl^- mg/L	Hg mg/L	Na mg/L	Ca mg/L
1S spring	4.55	418	1.45	6.49	7.56	349	43	18	12.50	111
1S summer	6.26	300	0.37	3.79	3.02	425	9.20	11.60	5.95	34.90
1S autumn	5.22	386	0.60	19	3.40	500	17	2.76	12	73.30
1S winter	5.78	316	1.32	7.82	1.40	680	18	2.16	39	121

(b)

Sample	Cr mg/L	Zn mg/L	Cd mg/L	Pb mg/L	Cu mg/L	Fe mg/L	Mn mg/L	Co mg/L	Ni mg/L	As mg/L
1Sp	4.78	20.98	10.10	0.11	1.62	5.03	5.12	2.16	1.49	8.94
1Ss	5.76	0.76	1.50	0.14	0.03	2.99	1.20	0.65	0.30	8.90
1Sa	6.50	1.24	1.10	0.63	0.10	12	5.32	0.97	0.08	3.28
1Sw	2.20	1	0	0.10	0.10	19.20	8.30	0.37	1.06	0.57

2.4 Impacts of acid mine drainage

Acid mine drainage effluents flowing through terrestrial ground into the water system negatively impacts the environment. Soluble metals present potential health and environmental risks arising from toxicity, which spread to resources of water such as streams, rivers, dams, lakes, and groundwater (Das *et al.*, 2009). Water contaminated by AMD, often contain elevated concentrations of chemical species. These results in the death of bottom-dwelling organisms in water resources and reduces the amount of gravel for fish to lay their eggs on, and hence affecting fish breeding (Pentreath, 1994). Jennings *et al.* (2008) revealed that several reports indicated low pH conditions, which alters the gill membranes of the fish or change gill mucus resulting in death due to hypoxia. Plant species that are found within and alongside AMD impacted water resources are endangered to a point of death. Most of them die due to their inability to survive in harsh conditions. AMD can also cause blindness on contact with eyes because it contains toxic chemical species (Akcil and Koldas, 2006, CSIR, 2013).

2.4.1 Environmental impacts

Acid mine drainage is significantly produced every time the sulphide minerals in mine tailings and other mine working are exposed to air and water. The major environmental concern with the gold and coal mine tailings is how they interfere with the land scape and contaminate the environment. Metal-rich acid mine drainage causes water resources to be undrinkable for human beings and too toxic for irrigation and other agricultural purposes (Simate and Ndlovu, 2014). This became evident when water from Boesmanspruit Dam in Carolina was too acidic (pH 3.7) and toxic for domestic use, and irrigation for several months, due to acid mine drainage run-off into the dam (McCarthy and Humphries, 2013; CER, 2016). This further affected aquatic ecosystem through species losses, impaired reproduction, declining biodiversity impaired ecosystem functioning and simplification of food webs (Byrne, 2012; McCarthy and Humphries, 2013; CER, 2016). Again, a decline in aquatic life and numerous animal mortalities was reported in Tweelopiespruit as a result of pollution caused by mining and attributed to the loss of water quality (Frost and Sullivan, 2011). A decline in population of benthic invertebrates and fish was also reported in other studies (Iwasaki *et al.*, 2009, Greig *et al.*, 2010).

A study by Durand (2012) showed that the water quality of the river systems, wetlands and groundwater has deteriorated noticeably over the past decade due to mine effluent issuing from mines in Gauteng and the North West Province. Similarly, DWS (2017) reported that mine water discharge from collieries in Mpumalanga province contains considerable number of potentially toxic metals, and radioactivity. As a result, the water quality of the receiving rivers, streams and wetlands has deteriorated significantly. Consequently, the deterioration of water quality has led to loss of riparian vegetation. The salinity of river systems that receive mine effluent is greatly affected by the volumes of sulphates contained in the AMD effluent (Durand, 2012). According to DWAF (2009) the mine effluent discharged from the Witwatersrand mine sites accounts for about 5% of the volume of water in the Vaal River but it accounts for about 20% of the salts entering the system. Acidified water seeping from the mine tailings dumps contributes an average of about 20% of stream flow from gold mine tailings in Johannesburg (Naicker *et al*., 2003).

In 2004 an estimate of 50 000m^3 of contaminated mine water was discharged into the Olifants River per day, with an additional 64 000 m^3 discharged from the abandoned collieries, hence Olifants River is regarded as the most contaminated river in Southern Africa (WWF-SA, 2011; CSIR, 2011). In the previous year's Eskom was extracting water from Olifants River catchment for power generation. However, the water quality has drastically deteriorated in the Olifants River, such that it can no longer be used in coal-fired power stations (CER, 2016). CER (2016) reported that throughout the years there have been large-scale fish dying in the Loskop Dam on the Olifants River catchment in Mpumalanga region. Scientists have concluded that this could be due to AMD from the collieries in eMalahleni (CER, 2016). Acid mine drainage has become a serious environmental concern in the country with regard to sustainable fresh water supply and fair distribution (McCarthy and Humphries, 2013). The potentially toxic metals and metalloids in AMD presents adverse effects that inhibit plant growth and development (Simate and Ndlovu, 2014). Mpumalanga was one of the significant producers of soya beans, maize, and dry beans, however, AMD has affected the quality of irrigation water and soil fertility, which compromised food production (BFAP, 2012).

2.4.2 Social-economic impacts

The potentially toxic metals persist in the natural environment for extended period and accumulate in successive level of the biological chain, hence causing acute and chronic diseases (Simate and Ndlovu, 2014). The metals accumulate in the vital organs and glands of human beings such as the heart, liver, kidney and brain, impairing their function and further inhibit absorption of necessary nutrients in their body (Simate and Ndlovu, 2014; Hota and Behera, 2015; Hendryx, 2015). When children specifically are exposed to AMD, their neurological, metabolic, and immune systems are devastated, and they appear *"missing"* mentally and are diagnosed as having autistic spectrum disorder (Smit, 2009). A study by CER (2014) was conducted on environmental rights training and a survey on human health in mining-affected communities such as Middleburg and Pullenshoop. The results of the latter study showed that 58% of people were suffering from poor health, while 64% were suffering from nausea, migraines or headaches, and several respondents had severe coughing, asthma and high blood levels with Pb and Cd. Several human diseases such as hypertension, Alzheimer's, psychiatric disorders, and birth defects have been linked to metal poisoning (Houston, 2011; Yorifuji *et al.*, 2011; Rubin *et al.*, 2011). As a result, DWA has set the guideline standards for the acceptable limit for potentially toxic metals in drinking water. Ecological and health impacts of certain elements contained in AMD are clearly stipulated in Table 2.3, as well as the DWA acceptable limit of those elements.

The government estimated a cost of R406.9 million to remediate AMD discharges from abandoned mines (Gigaba, 2018). Gordhan (2011) as the Minister of Finance, announced that R3.6 billion was assigned to water infrastructure and services, including funds to address AMD in the medium-term. This suggests that the problems of water contamination with AMD is costing our government a fortune. AMD increases the risk of ground deformation and attack structures made by human beings such as concrete building foundations, the liners of landfills and waste dumps (Naidoo, 2017). Cradle of Humankind World Heritage Site and other tourism sites are threatened and may be destroyed by the acidic nature of AMD (Jordan, 2015). Acid mine drainage is also degrading the soil fertility in agricultural areas. Naidoo (2017), reported that farming used to be very profitable until the land was contaminated with AMD, which led to acidification of the soil and a decline in soil fertility.

Table 2.3: Effects of selected metals on the health of living organisms (Tutu *et al*., 2008; Mohapatra *et al.,* 2011; Rubin *et al*., 2011).

Element	DWA limit	Ecological impacts of acid mine drainage
Al	< 0.5 mg/L	Prolonged exposure to aluminium has been implicated in chronic neurological disorders such as *dialysis dementia* and Alzheimer's disease. Severe aesthetic effects (discolouration) occur in the presence of iron or manganese
Fe	< 1 mg/L	Severe aesthetic effects (taste) and effects on plumbing (slimy coatings). Slight iron overload possible in some individuals. Chronic health effects in young children and sensitive individuals in the range 10 - 20 mg/L, and occasional acute effects toward the upper end of this range.
Mn	< 0.2 mg/L	Very severe, aesthetically unacceptable staining. Domestic use unlikely due to adverse aesthetic effects. Some chance of manganese toxicity under unusual conditions.
Cu	< 1 mg/L	Gastrointestinal irritation, nausea, and vomiting. Severe taste and staining problems. Severe poisoning with possible fatalities. Severe taste and staining problems
Mg	< 200 mg/L	Water aesthetically unacceptable because of bitter taste users if sulphate present. Increased scaling problems. Diarrhoea in most new consumers
Zn	< 5 mg/L	Bitter taste; milky appearance. Acute toxicity with gastrointestinal, irritation, nausea, and vomiting. Severe, acute toxicity with electrolyte disturbances and possible renal damage

2.5 Acid mine drainage remediation technologies

Treatment methods for AMD can be categorized into passive and active treatments (Trumm, 2010). This section will briefly discuss passive and active methods as well as their advantages and disadvantages.

Selection between active and passive treatment

There are several factors that influences the decision as to whether to use active or passive treatment (Figure 2.1).

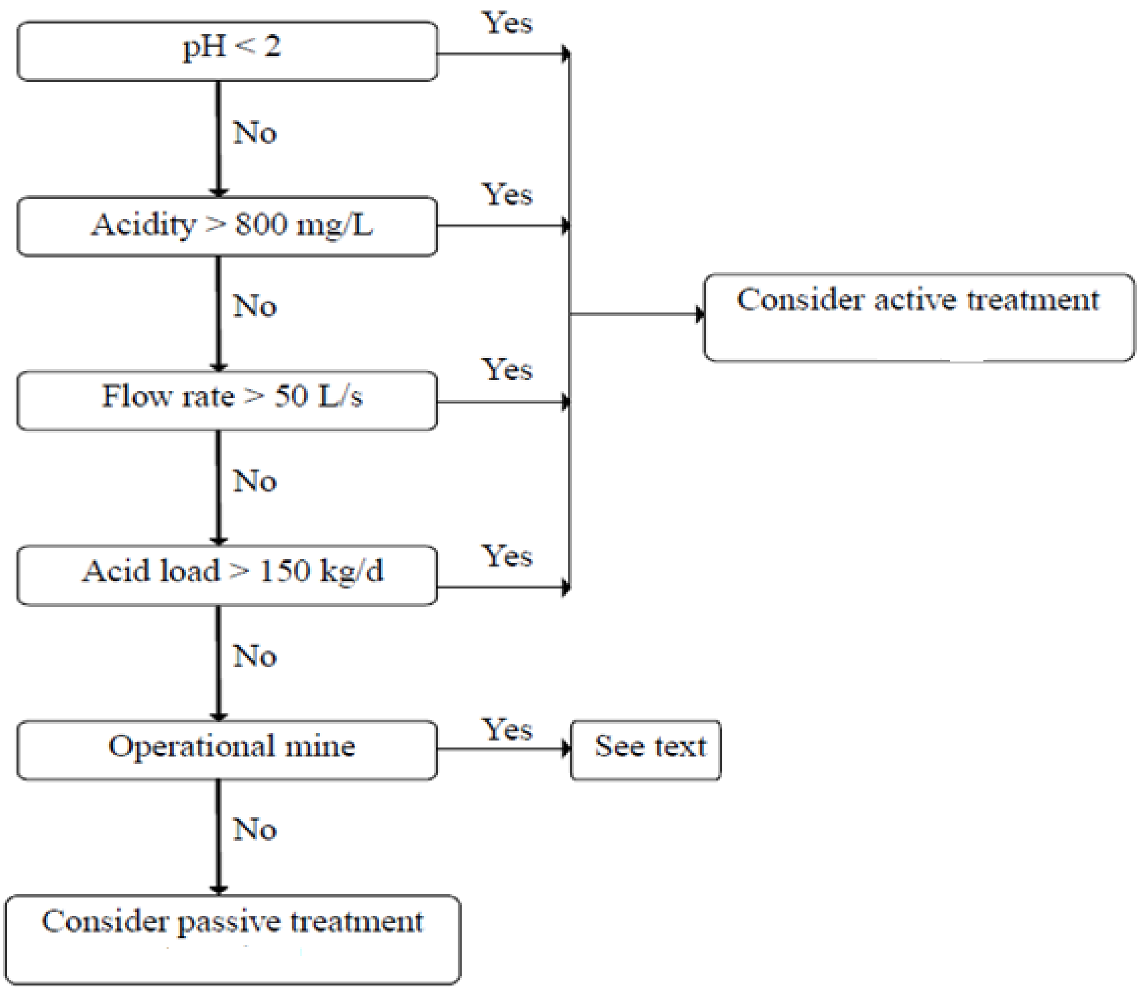

Figure 2.1: Factors to consider when selecting treatment methods (modified from Trumm, 2010).

2.5.1 Passive treatment

Humphries *et al.* (2017), defined passive treatment as passing water through an environment where geochemical and biological processes assist in improving the quality of the mine water and require relatively little resource input once in operation.

Passive systems present an advantage of being self-sustaining with sporadic maintenance, very low operating, and capital costs (Bwapwa, 2017). According to Humphries *et al.* (2017), passive treatment systems are commonly applied in cases of low AMD flow rates to enhance removal of sulphates and chemical species. Examples of passive treatment technologies include limestone/lime neutralisation, diversion Wells Sedimentation, anoxic limestone drains (ALD), successive alkalinity-producing systems (SAPS), reducing and alkalinity producing systems (RAPS), vertical flow reactors (VFR), and constructed or natural wetlands. This study focused more on natural wetlands as remediating system of AMD, and more details on this was explained below:

Wetlands as passive remediating system.

Natural wetlands have the ability to tolerate and eventually remediate acid mine drainage with very high acidity and high concentrations of dissolved metals (RoyChowdhury *et al*., 2015). This is achieved through the action of plants which reduces the water flow, mediating a degree of bulk metal extraction into biomass, enhancing input of organic carbon, including organic acids, and oxygen into the sediment to drive geochemical and biochemical reactions that lead to the formation of metal precipitates and alkalization (Beining and Otte, 1996; August *et al.*, 2002; Jacob and Otte, 2003; Dean *et al.*, 2013). In addition, metabolism of organic matter, which is abundant within the wetland, together with low oxygen availability, leads to reducing conditions that changes the distribution and speciation of metals within wetland sediments (Machel, 1989; Bigham *et al*., 1990; Fredrickson *et al*., 1998; Oueslati *et al.*, 2019).

In a wetland there are several processes that aid in remediation of AMD, these processes include physical, chemical and biological. Sedimentation and settling are the most efficient physical processes known for the elimination of chemical species in wetland water (Javed *et al.*, 2019). Wetland plant species offers resistance and serves as a sediment ploy (RoyChowdhury *et al*., 2015; Javed *et al.*, 2019). Chemical processes are divided into sorption, adsorption, precipitation and coprecipitation. Sorption is shifting of ions from water to the sediments and adsorption and precipitation aid in sorption of the contaminant (Javed *et al.*, 2019). Furthermore, cation exchange and chemo-sorption are known to be responsible for the adsorption of chemical species into the wetland sediments. However, adsorption of chemical species in organic matter is by means of electrostatic magnetism (Javed *et al.*, 2019). Precipitation is a conversion mechanism that limits the bioavailability of the chemical species through the formation of insoluble chemical species precipitates (Javed *et al.*, 2019)

The geochemical nature of the solution determines whether there will be metal uptake through adsorption process (Skousen *et al.*, 2017). Acidic nature of the solution favours high mobility and high solubility of the chemical species whereas alkalinity nature is the opposite. Under lower pH (<5) condition, there is precipitation of hydroxide, and due to high affinity, there will be high adsorption of chemical species into the precipitate. All hydroxide minerals are known to have high affinity as compared to other oxide minerals (Skousen *et al.*, 2017). The stability of the precipitate depends on the pH, such that when the pH decreases, the adsorbed chemical species into hydroxide precipitate will be released into the solution (Smith *et al.*, 2001). However, when the solution is alkaline (pH >8), alkaline precipitates (carbonate) will be formed. Alkaline environment represents the insolubility and unavailability of chemical species.

Acid mine water rich in sulphate, sulphate reducing bacteria generates hydrogen sulphide (Javed *et al.*, 2019). Chemical species (Me) occurring within the acid mine drainage reacts with hydrogen sulphide to form highly insoluble metal sulphide (Jha *et al.*, 2016), as clearly illustrated by Eq.2.6. Chemical species produces carbonates when they react with water high in bicarbonates, in the presence of limestone. Carbonate precipitation is operative for elimination of nickel and lead (Li *et al.*, 2016). The sulphate reducing bacteria obtains energy from carbon in organic matter (CH_2O) to convert sulphate to sulphide as shown by chemical reaction in Eq.2.5. The carbonaceous precipitates produced eventually increases the alkalinity of the water.

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3{}^{-} \tag{2.5}$$

$$Me^{2+} + H_2S + 2HCO_3 \rightarrow MeS + 2H_2 + 2CO_3{}^{2-} \tag{2.6}$$

Metals can be removed from AMD by precipitation and sorption. Iron and aluminium precipitates as hydroxides (Eq.2.5), whereas Mn is removed by a combination of oxidation and precipitation as illustrated in Eq.2.7.

$$Mn^{2+} + \frac{1}{2O_2} + H_2O \rightarrow MnO_2 + 4H^{+} \tag{2.7}$$

Other mechanisms that are responsible for the removal of metals include sorption, coprecipitation and exchange to precipitated Fe and Mn, organic materials and soil material are additional mechanisms for metal removal (Smith *et al.*, 2001; Skousen *et al.*, 2017). Over time, sulphate reduction is among the most important of the remediation processes taking place in AMD wetlands because it facilitates the fixation of metals by continuously generating alkalinity and maintaining pH in a favourable range for metal precipitation (Smith *et al.*, 2001).

2.5.1.1 Advantages and disadvantages of passive treatment methods

Almost all the methods used are cost-effective since natural materials are used. The methods are self-operating, hence constant monitoring is not necessary. Passive methods provide a long-term solution to AMD. They require large surface area in order to treat more AMD. However, they do not cope well with higher flow rates, because the methods of up-taking of pollutants or remediation are slow.

2.5.2 Active treatment

Active treatment is when the water is treated in a constructed plant where processes are controlled. This requires continuous input of resources to sustain the process. The range of application is adapted to all flow rates especially high flow rates (Bwapwa, 2017). Though operating and capital costs can be higher, the quality of effluent is very high with some potential for cost recovery by the sale of product water, metals, and by-products, and this can be considered as a great advantage over passive treatments (Nleya *et al.*, 2016). Active water treatment methods require the use of chemicals, while some require electrical and mechanical sources to perform efficiently. Vadapallia *et al.* (2008), revealed that one of the widely used and well-accepted active methods of treating acid mine drainage in South Africa is neutralization with lime (CaO) or limestone ($CaCO_3$). Some of the examples of active treatment methods that are used in South Africa are ion exchange, reverse osmosis, desalinization and electro dialysis.

2.5.2.1 Advantages and disadvantages of active treatment methods.

Relatively all the active methods require less surface area as compared to passive methods. This simply suggests that the space occupied by instrumentation used in active methods is less as compared to space of wetlands used in passive methods. Active methods have greater capacities to treat more wastewater. They have high flexibility such that they are able to treat any acidity. The most limiting factor of active methods is the high operating costs involved in purchasing the instruments or machines and chemicals required. Well informed and skilled operators are required to operate the expensive instrumentation. However, these methods don't provide a long-term solution to acid mine drainage. Furthermore, there is a problem with disposal of waste sludge produced during treatment process.

2.6 Natural wetlands and their performance in remediating AMD

Natural wetlands are used to remediate AMD, however, in the absence of natural wetlands, artificial wetlands are constructed. Common wetland plant species that are used worldwide and here in South Africa include *Phragmites, Juncus, Scirpus* and *Typha (*RoyChowdhury *et al*., 2015). These plant species are known to regulate the water flow, maintain microbial population and also accumulate the chemical species in water (Johnson and Hallberg, 2005; Skousen and Ziemkiewicz, 2005). There are two major mechanisms that wetland plants species use to remove chemical species from AMD such as phytoextraction and rizhofiltration (RoyChowdhury *et al.*, 2015). Where phytoextraction is the process whereby metal-hyperaccumulating plants uptake chemical species from wetland substrate and store them in their root and/or shoot. Whereas rhizofiltration is mechanism whereby plants adsorb or precipitate metals in the root zones (rhizosphere).

Plants such as *Typha latifolia, Scirpus validus*, *Phragmites australis* and *Oryza sativa* form plaques in their root epidermis by producing metal oxide and hydroxide precipitates that prevent the translocation of metals in the plant tissues (Snowden and Wheeler, 1995; Karathanasis and Johnson, 2003; Nyquist and Greger, 2009). RoyChowdhury *et al.* (2015) reported that *Typha latifolia* accumulated 29-59% of Al (aluminium) and 26 mg/kg of Cd was accumulated by *Juncus usitatus*. Furthermore, *Typha latifolia* showed greater Al and Fe retention in the roots as compared to other plant structures, whereas the accumulation of manganese is more in the above ground structures (stem/leaves) (Karathanasis and Johnson, 2003). These authors also reported that *Scirpus validus* had higher affinity of aluminium in higher soluble metal concentration whereas *Typha latifolia* had higher affinity of aluminium in lower soluble metal concentration. A study conducted by He and Yongfeng (2009) on bioconcentration of heavy metals by *Phragmites australis* cultivated in synthesized substrates showed that *Phragmites australis* had higher accumulation of metals (Fe, Mn, Al, Cd) in the root system as compared to other parts of the plants.

2.8 Metal accumulation efficiencies

A low soil pH causes leaching of bio-essential elements (e.g., Ca, Mg) and excessive uptake of potentially phytotoxic elements (e.g., Al, Mn) (Yang *et al.*, 2016). Plants inhabiting AMD-impacted areas are metal-tolerant species (metallophytes). Yang *et al*., 2016 reported the differences in element concentration in plant samples observed in two sampling periods can be explained by a diverse impact of the AMD waters on plants growing in nine sampling sites and by interspecies differences in the abilities of element uptake and translocation to the above-ground organs. Bioconcentration factor (BCF) and translocation factor (TF) can be used to classify plants as hyperaccumulators of toxic metal species, thereby estimating a plant's potential for phytoremediation purpose (Yoon *et al.*, 2006; Sun *et al.* 2009). Bioconcentration factor is defined as an index of the plant's ability to accumulate a particular metal concerning its concentration in the soil and or water (Abdul and Thomas 2009). Hyperaccumulator plants should have a BCF of greater than one (Li *et al.,* 2007), for efficient phytoextraction purposes translocation factor should be greater than one (Bazihizina *et al.*, 2015). High TF values indicates that metals were translocated from the roots to the shoots, which is advantageous during harvesting time (Kamari *et al.*, 2014).

Conclusions

Gold mine tailings are associated with potentially toxic metals and metalloids that leads to negative environmental and health impacts. It was also indicated that these mine tailings are a source of pollution and a major contributor of AMD. The communities surrounding the Crown Gold Mine tailings, are subjected to respiratory health problems due to dust emanating from the mine tailings. This dust also affects the drivers on the roads of Soweto and towards FNB stadium. The leachates are contaminating the neighbouring water resources and the agricultural land. On the other hand, communities of Mpumalanga are affected by acid mine drainage which is compromising their available freshwater resources. As a result, the supply of clean water has been compromised in Witbank area, such that tap water is not safe for drinking. Furthermore, it is contaminating the arable land through acidification and inorganic contaminants enrichment in the soil, which deteriorates the fertility of the soil.

There are different techniques of AMD remediation, however this study focused more on passive treatment method. Amongst all the studies conducted using wetland plant species to remediate AMD, few studies identified native plant species. Most of the studies used the world-wide dominant plant species (as *Phragmites australis, Juncus effusus, Typha latifolia* and *Scirpus lacustris*). According to the observations made by Mabhena (2015), the selection of wetland plant species for the past decades has been biased worldwide, while there is vast biodiversity of wetland plant species that may have the potential to remediate AMD. The use of invasive plant species such as *Phragmites australis, Typha latifolia* and *Scirpus lacustris* in constructed wetlands were beneficial in the retention of AMD pollutants or chemical species. However, since they are invasive, they grow rapidly and dominate the wetlands and other neighbouring areas, consequently replacing native species and destroying habitat for other organisms. According to Rezania *et al.* (2019), *Phragmites australis* leads to deterioration of water quality in constructed wetlands through blocking the water flow. Furthermore, *Phragmites australis* leads to an increase in sediment deposition in the wetland, which subsequently results in a reduction of the wetland volume and its capacity to store water.

The main focus of this study was to identify naturally growing plant in gold mine tailing and South African native plant species in wetlands, streams, and mine water discharging points. The identified plant species were assessed for bioconcentration of chemical species in different parts of the plants. Furthermore, investigation of chemical composition of the gold mine tailings, and mine water as the sources of chemical species, sediments, and aqueous samples from the wetland. The role of plants, sediments and geochemical process that are responsible for the remediation of AMD are therefore be elucidated.

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Chapter 3: Physicochemical Characterization of abandoned Crown Gold Mine tailings and leachates: Assessing the phytoextraction potential of inorganic chemical species by *Cortaderia selloana and Populus alba*.

Abstract

Abandoned mine tailings often generate acidic leachates that contains high concentration of inorganic chemical species that contaminates surface and groundwater. This chapter aims at evaluating the physicochemical properties of the abandoned Crown Mine gold mine tailings located in Johannesburg, South Africa and their acidic leachates. Furthermore, evaluate the potential of using *Cortaderia selloana* and *Populus alba* in phytoextraction of inorganic chemical species from mine tailings. Physicochemical parameters such as pH, EC, TDS, were determined using pH/EC/TDS multi-meter, while cations were determined with inductively coupled plasma mass spectrometry (ICP-MS), laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) and x-ray fluorescence (XRF) was used to determine the major oxides in mine tailings, and anions were determined with ion chromatography (IC). The results showed that the mine tailings are mainly composed of SiO_2, Al_2O_3, Fe_2O_3 and K_2O as major oxides and elements such as Tb, Ta, Tm, Mo, Eu, Lu, Ho and Cs as trace elements. The pH, EC, TDS of the leachates were found to be ranging from 3.31 to 5.21, 3 857 to 5 517 mS/cm and 1930 to 2704 mg/L, respectively. The leachate samples were characterized by higher concentrations of Mn, As, Cr, Al, Pb, Ca, Na, K and Fe. The most dominating anions within the leachates were Cl^- and SO_4^{2}. *Cortaderia selloana* and *Populus alba* accumulated high concentrations of Mn, Zn, P, Mg, K and B in their leaves as compared to other parts of the plant. The translocation factor (TF) reflected that *Cortaderia selloana* plant species have the potential to translocate all the chemical species from the roots to the shoots except for selenium (Se). Moreover, *Cortaderia selloana* showed bioconcentration factor greater than 1 for chemical species such as B, Mn, Zn, Sr, Ca, Mg, P, and Si indicating the potential for use in phytoextration of these chemical species from mine tailings. Similarly, *Populus alba* showed the bioconcentration greater than 1 for Mn, Ni, Cu, Sb, Na and Mg showing the potential use for phytoextraction of these species. In addition,

Populus alba showed bioconcentration factor greater than 10 showing hyperaccumulation ability for species such as B, Co, Zn, Ca, Cd, K, P and Sr. Overall findings of this chapter showed that *Populus alba* and *Cortaderia selloana* have potential for use in phytoextraction of inorganic chemical species from the gold mine tailings and are recommended for phytoremediation of these tailings.

Keywords: *Bioconcentration, toxic species, leachate ponds, mine tailings, Cortaderia selloana, Populus alba*

3.1 Introduction

The Witwatersrand basin of South Africa is well-known for its gold mineralisation. As a result, Johannesburg is referred to as the city of gold and consequently, it was developed due to mining activities (Naicker *et al.,* 2003). However, these mining activities produce mine wastes or mine tailings (Oyourou *et al.*, 2019), of which they are a source of environmental problems all over the world and they are increasing daily (Naicker *et al.*, 2003; Wang *et al.*, 2011; Keshri *et al.*, 2015; Sibanda *et al.*, 2019). The contamination of the natural environment can result from erosion of mine tailings either by wind or water, whereby toxic chemical species will be transported into water sources and agricultural land (Dold and Fontboté, 2001; Tutu *et al.*, 2008; Fashola *et al.*, 2016; Naveen *et al.*, 2018; Wang *et al.*, 2019). The water quality of the river systems, wetlands and groundwater have deteriorated noticeably over the past decade due to mine effluent from mines in Gauteng and the North West Province (Durand, 2012). The mine effluents accounts for about 20% of the salts entering the water system (Naicker *et al.*, 2003; DWAF, 2009). Exposure to high concentration of potentially toxic chemical species above the tolerance limit stipulated by World Health Organisation (WHO) may result in health impacts such as lung diseases, bronchitis, bones softening, cardiomyopathy and kidney damage (Redwan and Bamousa, 2019)

In order to minimize the environmental impacts associated with mine tailings, there has been a noticeable increase in studies focusing on rehabilitation of mine tailings in South Africa (Anawar, 2015; Wang *et al.*, 2017; De Simoni and Leite, 2019; Nyenda *et al.*, 2020). Different methods and techniques commonly used for the remediation of mine tailings include stabilization and solidification, capping, and phytoremediation (Wang *et al.*, 2017; Park *et al.*, 2019; Kiventera, 2019). Phytoremediation is the technology that uses plant species to stabilize and or remove toxic metals from the soil or water. This technology has several advantages such as cost-effectiveness, environmentally friendly, attenuation of toxic metals, erosion, and dust control (Karaca *et al.*, 2018). Phytoremediation has been in metal contaminated soils, mine tailings and wastewater, and it has been proved to be effective (Naicker *et al.*, 2016; Schachtschneider *et al.*, 2017; Wang *et al.*, 2017; Siebert *et al.*, 2018; Przybylowicz *et al.*, 2020).

Phytoextraction is translocating and concentrating metal pollutants into the aerial harvestable parts (Xu *et al*., 2019). Translocation and bioconcentration are factors that are used to estimate a plant's potential to be used in phytoremediation (Lam *et al*., 2017). Translocation factor (TF) indicate the ability of the plant to translocate the metals from the roots to the shoots, and for efficient phytoextraction purposes, translocation factor should be greater than 1 (Bazihizina *et al.*, 2015). Bioconcentration factor (BCF) reflects a plant's ability to accumulate metals concerning their concentration in the soil and or in water (Hladun *et al*., 2015; Kandziora-Ciupa, 2017). When the BCF, value is greater than 1, then the plant species is suitable for use in phytoextraction of that particular metal species. Moreover, when the value is greater than 10 plants is considered to have hyperaccumulation potential of specific metal species (Rezvani and Zaefarian, 2011).

The capacity of different plant species such as *P. australis*, *T. capesis*, *S. corymbosus, J. usitatus* and *J. effuses* has been evaluated by RoyChowdhury *et al.* (2015) and; Schachtschneider *et al.* (2017) for their bioconcentration of Al, Fe and Mn in the Upper Olifants River. Their results showed that both species have bioconcentration capacity towards Al, Fe and Mn and further indicated that they has potential for application in phytoremedation. A study by Przybylowikz *et al.* (2004) conducted at Barberton area in Mpumalanga province, showed that *Bierkheya coddii* has the potential to accumulate more toxic chemical species (Ni, Fe, As, Zn, Na, Co, Br, Cd, Pb) from tailings and wastewater. Gumbo *et al.* (2009) identified four grass species (*Paspalum dilatatum, Cynodon dactylon, Cyperus esculentus and Hypparrhenia hirta*) growing in gold mine tailings of New Union mine at Malamulele village and determined their bioaccumlation potenial towards inorganic contaminants. The results showed that *Cynodon dactylon* had greater potential in bioconcentration of Co,Cd,Cu,Zn and Mn, followed by *Cyperus* esculentus. *Hyparrhenia* had hyperaccumulation of Cu and Zn, while *Paspalum dilatutum* had the least accumulation of all investigated metals. Based on the bioconcentration coefficient, all the identified grass species were reported to be hyperaccumulators of toxic chemical species Co, Cd, Cu, Zn and Mn.

The current study area covers three gold mine tailings dumps of Crown mine within the Central Rand of the Witwatersrand basin. The area is characterized by fine grained mine tailing and leachates from the mine tailings which are retained in the ponds for treatment purposes. There are numerous studies on characterization of Gold mine tailings and phytoremediation in Witwatersrand, however, only a few focuses on phytoremediation (Nengovhela *et al*., 2006; Mulungisi *et al*., 2009; Bakatula, *et al*., 2012; Yalala, 2015; Hansen, 2018; Netshiongolwe, 2018). There are no studies in Witwatersrand that have evaluated *Cortaderia selloana* and *Populus alba* that are naturally colonizing Crown Mine tailings dumps for their potential uptake of metals. Therefore, this present study focuses on characterizing physicochemical properties of mine tailings and leachates from Crown gold mine tailings dump and further evaluate the potential of *Cortaderia selloana* and *Populus alba* in the accumulation of inorganic contaminants. *Cortaderia selloana* is characterized as a grass/sedge type of species, while *Populus alba* is characterized as a shrub. These were the only two plant species identified which were naturally colonizing the gold mine tailings.

3.2 Description of the study area

The study was conducted in Crown Gold Mine within the Witwatersrand basin in Gauteng region, South Africa. The mine lies within the longitude and latitude of 27°57’0” to 27°59'30"E and 26°14’30” to 26°13'0"S as indicated in Figure 3.1. The study area is situated on the Highveld plateau, which is characterised by a temperate climate, with winter temperatures ranging between an average of 4.1°C to 16°C and summer temperatures varying from an average of 14.7° to 25.6°C (Weather atlas, 2021). The area receives annual rainfall ranging between 600 to 700 mm mainly in summer (Mabhena, 2012).

The area is characterised by a well-defined drainage system including streams and wetlands which form the tributaries of the upper Klip River and flows into the Vaal River, from which Johannesburg obtains the bulk of its water supply (Tutu *et al*., 2008). Geologically, the area is dominated by arenaceous sequence comprised of quartz-pebble conglomerates, quartzites, quartzwackes with polymitic clasts and minor shales (Turker *et al.*, 2016). The origin of the huge amount of gold is largely confined to conglomerate layers (Rainier *et al.*, 2020). Pyrite is present in the gold-bearing conglomerates in certain quartzites and is often enriched in gold (Turker *et al.*, 2016). Figure 3.1 shows the map of the study area and the sampling points.

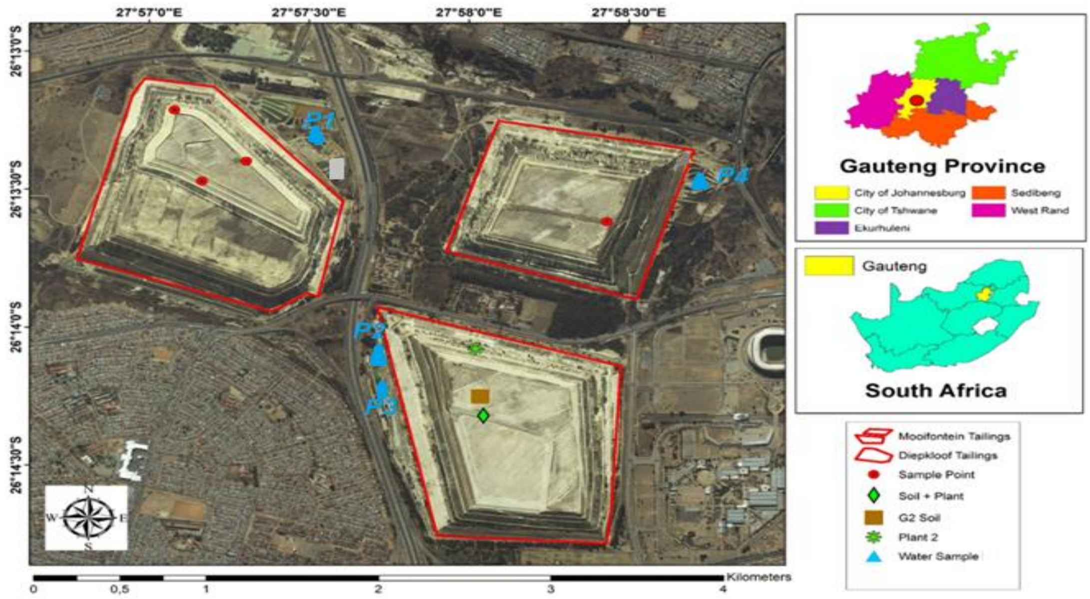

Figure 3.1: Study site and sampling points.

Crown Mine was founded in 1909, they produced over 80 tons of gold in a day, but by the 1950s its reserves had been depleted. The original mining plans of 1890s were the key to extending the exploration and kept the Crown Mines active. The gold deposit in the Witwatersrand Crown Mine finally closed in 1976. The company then made efforts to extend the life of the mine through re-opening old shafts, re-mining old stopes and rehabilitating abandoned areas (Moodie, 2005). The mine produced tonnes of waste which were dumped in Diepkloof and Mooifontein. The Diepkloof mine tailings are the oldest dating up to 30 years, and the Mooifontein dumps are much younger. However, the Mooifontein1 mine tailings occupy the largest surface areas which is approximately 146 hectares, followed by the Diepkloof with 130 hectares and lastly the Mooifontein2 mine tailings located at the North-western side of the FNB stadium which covers approximately 89 hectares on the ground.

The Crown Mines are making efforts to rehabilitate all three mine tailings dumps by planting grasses and trees around and on top of the mine tailings. Figure 3.2 indicates the rehabilitation activities happening on the mine tailings. The water retained within the tailings ponds are treated before they can be reused, e.g., cooling equipment and for irrigation.

Figure 3.2: Rehabilitation and retention of the leachate activities, a drainage pipe, b dust control, c leachate retention ponds and d vegetation cover.

3.3 Materials and methods

3.3.1 Mine tailings, water, and plant sampling

Samples of mine tailings, mine leachates and plant species were collected from different points as indicated in Figure 3.1. Gold mine tailings were collected using a hand auger at 1 meter depth. Sample sites were selected randomly considering the colour and texture of the mine tailings. Table 3.1 shows the sample ID, GPS coordinates, location, and brief description of the sampling point.

Table 3.1 Sampling points, location, GPS coordinates, and brief description of the location.

Sample ID	Coordinates	Location	Description
P1	26°13'23.3" S 27°57'34.4" E	Diepkloof	Mine tailings retention pond
P2	26°14'15.7" S 27°57'44.2" E	Mooifontein1	Mine tailings retention pond
P3	26°14'15.8" S 27°57'45.6" E	Mooifontein2	Mine tailings retention ponds
P4	26°13'23.3" S 27°58'41.2" E	Mooifontein2	Mine tailings retention ponds
G1	26°13'24.4" S 27°57'17.5" E	Diepkloof	On-top of the mine tailings dump
G2	26°14'18.6" S 27°58'02.7" E	Mooifontein1	On-top of the mine tailings dump
G3	26°14'18.9" S 27°58'23.9" E	Mooifontein2	On-top of the mine tailings dump
K1	26°14'18.6" S 27°58'02.7" E	Mooifontein1	On-top of the mine tailings dump
K2	26°14'17" S 27°58'02.7" E	Mooifontein1	On-top of the mine tailings dump
K3	26°14'18.1" S 27°58'25.1" E	Mooifontein2	On-top of the mine tailings dump

A total of 8 samples of mine leachates were collected from the leachate's retention ponds around the mine tailings using HDPE plastic bottles which were pre-cleaned with distilled water and rinsed with 3 M nitric acid (Tutu *et al.*, 2008; RoyChowdhury *et al.*, 2015). Physicochemical parameters such as pH, EC, Eh, DO, TDS and salinity were determined in the field using pre-calibrated Thermo Scientific Orion Star A324 pH multi-meter (Waltham, Massachusetts). Leachates samples were collected in pairs with one designated for metal cations and the other for anions. Samples for cation analysis were acidified with 3 M HNO_3 prior to storage in a cooler box with ice and then transported to the laboratory where they were stored at temperature <4 °C till analysis. Figure 3.3 shows the identified plant species growing on mine tailings. A total of three plant samples, two for *Cortaderia selloana* (sample K1 and K2) and one for

Populus alba (K3) were collected in Mooifontein tailings dumps. Plants were uprooted using a garden spade and stored in sealable plastic bags

Figure 3.3: Identified plant species growing on gold mine tailings, Gauteng, a *Cortaderia selloana and b Populus alba*.

3.2.3 Physicochemical and elemental analysis

The detailed elemental composition of the mine tailings, water samples and plants were carried out using Agilent 7900 Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICPMS) (Santa Clara, CA), X-ray florescence (XRF) Agilent 7700 (Santa Clara, Ca) and Agilent 7900 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Santa Clara, CA) respectively, at central analytical laboratory of Stellenbosch University. Anions were determined using Metrohm 850 professional Ion Chromatography (IC). Before analysis, mine tailings were air-dried and then milled into homogeneous powder using Retsch RS 200 Vibratory Disc Mill (Duesseldorf, Germany). Mine tailings were further digested using the aqua regia method following the procedure described by Joseph *et al.* (2017).

Plant samples were separated into different parts (roots, leaves, and stem) and washed with deionized water to remove excess soil. Washed samples were then air-dried for a day and then oven-dried at 80 ^{o}C for 4 days. Dried plant samples were ground into powder using a coffee bean grinder (Sunbeam, Chicago, USA) and thereafter digested using the aqua-regia method as described by Joseph *et al.* (2017).

3.2.4 Metal accumulation potential in plants

The metal accumulation potential was assessed by calculating the bioconcentration factor and translocation factor. Bioconcentration factor (BCF) and translocation factor (TF) of different metals from soil to plants were calculated based on the dry weight of plant samples. The following equations were used:

$$BCF = \frac{\boldsymbol{C}plant\ organ}{\boldsymbol{C}mine\ tailings} \qquad 3.1$$

$$TF = \frac{\boldsymbol{C}shoot}{\boldsymbol{C}roots} \qquad 3.2$$

C- representing the mean concentration of the plant tissue/ mine tailings

Plant organ- representing leaves/stem/root (whole plant)

3.4 Results and discussion

3.4.1 Physicochemical characterization of the mine tailings

Table 3.1A shows major oxides of the gold mine tailings analysed using XRF (see Annexure 1). Table 3.2 depicts the physicochemical parameters of the gold tailings determined from the tailings paste (pH and anions) and digested samples (chemical species).

Table 3.2: Physicochemical parameters of the mine tailings.

Physicochemical properties (mg/kg)	Diepkloof G1	Mooifontein1 G2	Mooifontein2 G3
pH	6.21	6.28	6.84
Cl^-	24.05	45.45	142.55
NO_3^-	6.05	14.35	11.15
SO_4^{2-}	1737.45	5237.70	6643.55
B	7.63	2.34	1.97
V	1.88	4.99	2.91
Cr	11.88	36.37	19.71
Mn	36.13	133.47	18.21
Co	5.12	21.10	1.63
Ni	9.83	51.20	5.49
Cu	15.34	37.08	7.13
Zn	10.94	56.38	10.32
As	36.05	83.26	34.12
Se	0.43	0.90	0.59
Sr	29.15	4.53	3.22
Mo	0.21	0.86	0.34
Cd	0.05	0.13	0.01
Sn	1.22	1.75	1.06
Sb	0.54	1.18	0.50
Ba	5.95	9.93	6.29
Hg	0.44	1.07	0.43
Pb	9.55	26.73	14.98
Al	994.80	2874.00	1142.00
Fe	4750.00	12826.00	6346.00
Ca	10114.00	3162.00	1535.40
K	84.02	210.40	101.90
Mg	524.20	1362.60	546.80
Na	195.54	1321.40	60.10
P	28.88	50.90	27.54
Si	333.20	512.40	436.60

From the results, it is noted that the paste pH of the mine tailings were ranging from 6.21 to 6.84, with a sample from Mooifontein2 having the highest pH (6.84). This pH is higher as compared to the pH (3.5-5.6) for gold mine tailings collected from Central Rand Group in Witwatersrand basin which was reported by Netshiongolwe (2018). Higher pH compared to the normal mine tailings could be attributed to neutralizing agent such as lime added to the mine tailings for rehabilitation purposes (Maree *et al.*, 2013; Li *et al.*, 2018). Anions such as chloride (24.05 to 142.55 mg/kg), nitrate (6.05 to 14.35 mg/kg) and sulphate (1737.45 to 6643.55 mg/kg) were detected in the mine tailings samples. The presence of nitrates could be due to added fertilizers for plant growth, while sulphates could be a result of the dissolution and leaching of sulphide minerals. Metallic chemical species such as Fe, Al, Mg, Si, Na, As, Mn, Zn, Cu, Sr, and Cr were detected in higher concentration with other toxic of Cd, Se, Sb, Mo and Hg detected at trace levels. These metallic chemical species are associated with minerals such as greenockite, cinnabar and sphalerite, calcite, and arsenopyrite. The mine tailings were dominated by major oxides such as SiO_2, Al_2O_3 and Fe_2O_3, with traces of K_2O, CaO, MgO, TiO_2, MnO, Na_2O and Cr_2O_3. These oxides are associated to some of the elements detected in the mine tailings such as Si, Al, Fe, Ca, Mg, Cr, Mn, Na and K. The environmental hazards associated with the latter metals are degrading water quality and soil fertility, poisonous to aquatic organisms, destroying terrestrial and aquatic biodiversity.

3.4.2 Leachate samples

Table 3.3 presents the physicochemical composition of mine leachates collected in the mine tailings retention ponds. The analysis of pH, EC, TDS, Eh, DO and salinity was done in the field, while another elemental analysis was done using ICPMS and Ion chromatography. The measured values for physicochemical parameters were compared to standard guideline for wastewater discharge as stipulated by DWAF of 1999.

Table 3.3: Physicochemical characterization of leachates from gold mine tailings ponds.

Physicochemical parameters	Diepkloof P1	Mooifontein1 P2	Mooifontein1 P3	Mooifontein2 P4	Wastewater Discharge Limit (DWAF)
pH	5.13	4.08	4.49	3.31	5.5-9.5
EC mS/cm	3 857	4 473	3 882	5 517	700-1500
TDS mg/L	1980	2175	1903	2704	
Eh mV	3 857	4 473	152.8	220.3	
DO mg/L	8.17	8.35	8.2	8.76	
Salinity psu	2.182	2.409	2.1	3.023	
Cl^- mg/L	148.41	135.97	159.11	201.28	0.25
Br^- mg/L	4.64	4.56	4.6	4.79	
SO_4^{2-} mg/L	59.39	61.7	62.65	62.21	
F^- mg/L	2.88	2.68	2.6	3.5	1
V µg/L	0.50	0.25	0.10	2.87	
Cr µg/L	12.39	14.31	13.58	49.19	10
As µg/L	20.08	9.29	18.90	16.76	20
Se µg/L	0.55	0.64	0.54	0.46	20.00
Sr mg/L	0.63	0.50	0.51	0.60	
Cd µg/L	0.21	0.37	0.34	0.93	5.00
Sb µg/L	0.05	*BDL	*BDL	0.06	
Ba µg/L	24.55	20.76	20.82	15.72	
Pb µg/L	0.49	14.14	1.45	2.03	10.00
Mn mg/L	9.38	18.80	14.87	24.03	0.1
Co mg/L	0.92	1.18	0.78	1.58	
Ni mg/L	0.69	0.72	0.54	2.38	
Cu mg/L	0.01	0.03	0.01	0.10	0.01
B mg/L	0.32	0.18	0.17	0.20	1.00
Zn mg/L	0.47	0.46	0.33	1.44	0.1
Al mg/L	8.7	14.8	11.5	37.5	
Fe mg/L	149.9	189.6	168.4	333.7	0.3
Ca mg/L	459.8	452.4	480.2	405.7	
K mg/L	50.9	35.9	25.5	40.7	
Mg mg/L	31.5	46.1	36.0	80.6	
Na mg/L	189.4	161.9	122.7	113.8	
Si mg/L	8.5	9.4	8.3	10.3	

From the results, it is noted that the leachates were acidic with pH ranging between 3.31 and 5.13. This pH was found to be below the wastewater discharge limit (DWAF, 1999). The pH levels could have drop due to neutralizing agents added to aid in phytoremediation process. A previous study conducted from the gold mine tailings in the Central Rand of the Witwatersrand showed a similar trend in the pH of the tailing ponds ranging from 3.5 to 5.6 (Netshiongolwe, 2018). Furthermore, positive redox potential (Eh) and dissolved oxygen (DO) values were measured ranging between 152.8 to 220.3 mV and 8.17 to8.76 mg/L, respectively. The highest Eh and DO was measured from sample P4, where pH had the lowest reading of 3.31. Acidic pH favours oxidation reaction process and hence positive redox potential values were measured. This resulted in higher concentration of dissolved toxic chemical species in mine leachates. The EC, TDS and salinity were found to be ranging between 3857 to 5517 mS/cm, 1980 to 2704 mg/L and 2.1 to 3.02 psu, respectively. The lowest concentration of the aforementioned parameters was noted in sample P3, while the highest was from P4, this could be due to evaporation and precipitation (Tutu *et al.*, 2008; Maya *et al.*, 2015; Grover *et al.*, 2015). There was evidence of precipitation on the site, causing minerals crust. Figure 4 shows the observed mineral crusts in the field.

a b

Figure 3.4: Mineral crust in leachate retention ponds, a and b shows the minerals crust on the surface.

The higher concentration of EC and TDS showed more dissolved salts in sample P4. Studies have shown that leachates with low values of pH mostly have higher concentration of total dissolved solids due to the acidic leachates dissolving more metals into the solution (Akcil and Koldas, 2006; Gaikwad and Gupta, 2008). It is noted that Fe, Ca, K, Na, Mg, Al, Si and Mn are the major elements dominating the leachate in the retention ponds, with Se, Sr, Sb, Cr, Cd, V, Pb, and Ba as trace elements. Similarly, the mine tailings were dominated by the same elements and this showed that the composition of the leachates originated from the mine tailings. The concentration of toxic chemical species such as Cr, Pb, Se, Mn, Zn and Fe in the leachates exceeded the wastewater discharge limit (DWAF, 1999). The excess concentration of these chemical species could result in chlorosis of the plant leaves and reduced growth, diarrhoea, gastro-internal distress, arthritis in organisms and human beings when ingested (Sedibe *et al.*, 2017).

3.4.3 Plant samples

Table 3.4 presents the elemental concentration of inorganic chemical species in roots, leaves, and stems of plant species. The elements were determined using ICP-MS in digested samples.

Table 3.4: Elemental composition detected in *Cortaderia selloana* and *Populus alba.*

Elementmg/kg	***Cortaderia selloana***				***Populus alba***		
	Leaves K1.1	**Roots K1.2**	**Leaves K2.1**	**Roots K2.2**	**Leaves K3.1**	**Stem K3.2**	**Roots K3.3**
B	9.19	2.15	8.26	2.41	71.3	15.22	25.07
V	0.18	0.03	0.24	0.15	0.37	0.1	0.17
Cr	13.82	2.24	12.97	20.47	5.13	4.83	7.08
Mn	196.96	14.9	169.15	66.87	117.55	34.98	72.15
Co	4.17	3.52	1.51	8.47	21.28	3.31	5.23
Ni	30.26	10.17	12.22	25.04	44.01	8.13	21.03
Cu	16.7	4.67	7.34	12.29	7.18	11.77	19.89
Zn	72.3	23.62	18.97	32.73	144.85	97.37	64.34
As	1.45	0.33	1.71	1.51	2.91	1.26	1.96
Se	0.04	0.06	0.04	0.02	0.04	0.02	0.03
Sr	5.04	2.74	4.07	3.28	6.4	6.04	35.66
Cd	0.07	0.05	0.02	0.04	0.2	0.23	0.15
Sn	0.02	0.01	0.02	0.02	0.01	0	0.02
Sb	0.02	0.01	0.02	0.02	0.01	3.12	0.03
Ba	1.81	1.25	1.77	1.44	2.88	1.77	5.46
Hg	0.05	0.05	0.05	0.06	0.06	0.06	0.07
Pb	0.99	0.13	0.48	0.4	2.77	7.4	1.22
Al	0.07	0.03	0.04	0.11	0.22	0.1	0.73
Fe	0.34	0.08	0.24	0.38	0.6	0.19	0.32
Ca	3.45	0.44	2.45	1.09	5.62	3.46	16.09
K	12.03	1.81	6.78	5.13	11.74	3.25	2.69
Mg	2.32	0.28	0.81	0.6	1.79	0.56	0.9
Na	0.09	0.03	0.01	0.07	0.05	0.04	0.36
P	0.45	0.1	0.22	0.43	1.47	0.65	0.89
Si	0.63	0.06	0.4	0.13	0.37	0.04	0.06

The results in Table 3.4 shows that *Cortaderia selloana* (K1) collected on top of Mooifontein tailings dump accumulated higher concentrations of Mn, B, Co, Cu, Zn, As, Ba, Ca, K, Mg, and Mn in the leaves of and elements such as Cr, Ni, Sr, Ba and Zn were largely accumulated by the roots. A similar trend was observed in the *Cortaderia selloana* (k2) collected approximately 50 m away from K2 in Mooifontein tailings dump. Traces of Pb, Cd, Al, Fe, and Si were noted in both *Cortaderia selloana* plant samples. The *Populus alba* showed higher accumulation of Mn, Co, B, Ni, Zn, As, K and Mg in the leaves, Pb in the stem, and Cu, Sr, Ba, Ca, and Cr in the roots. Traces of Si, Na, Fe, Al, Sb, Sn, Se and V were accumulated in the different plant tissues of *Populus alba.* The results obtained shows that both species have the potential to extract chemical species from the soils and translocate them from the roots to the shoots. As a result, these plant species can be used in remediation of mine tailings and other chemical contaminated soils. *Cortaderia selloana* and *Populus alba* plant species showed a higher concentration of toxic chemical species (Mn, B, Zn, Sr, Ni, Ca, K, Mg, P and Si) as compared to the mine tailings collected next to the plant and this could be an indication that these plants species were able to extract those chemical species into their tissues.

3.4.4 Translocation and Bioconcentration factor of metals in plant species

Translocation factor (TF) indicated the ability of the plant to translocate the metals from the roots to the shoots. For efficient phytoextraction purposes, translocation factor should be greater than one (Bazihizina *et al.*, 2015). Bioconcentration factor (BCF) reflects a plant's ability to accumulate a particular metal concerning its concentration in the soil and or in water (Hladun *et al.*, 2015; Kandziora-Ciupa, 2017). If the BCF value is greater than 1, then the plant species is suitable for use in phytoextraction of that particular metal species. Moreover, when the value is greater than 10 plant is considered to have hyperaccumulative potential towards the metal species (Rezvani and Zaefarian, 2011). Table 3.5 shows the translocation factor and Table 3.6 shows bioconcentration factor.

Table 3.5: Translocation factor (TF) of toxic chemical species in *Cortaderia selloana* and *Populus alba*.

Cations	***Cortaderia selloana* K1**	**Cortaderia selloana K2**	***Populus alba* K3**
B	4.271	3.428	3.450
V	5.331	1.552	2.886
Cr	6.169	0.634	1.408
Mn	13.223	2.530	2.114
Co	1.183	0.179	4.697
Ni	2.977	0.488	2.479
Cu	3.579	0.597	0.952
Zn	3.061	0.580	3.765
As	4.474	1.136	2.126
Se	0.758	2.170	1.901
Sr	1.837	1.238	0.349
Cd	1.565	0.520	2.783
Sn	1.768	1.039	0.540
Sb	1.608	1.126	103.076
Ba	1.442	1.229	0.852
Hg	1.023	0.812	1.654
Pb	7.589	1.191	8.351
Al	2.617	0.364	0.444
Fe	4.172	0.620	2.488
Ca	7.904	2.249	0.564
K	6.666	1.321	5.574
Mg	8.330	1.346	2.604
Na	2.674	0.096	0.229
P	4.389	0.522	2.386
Si	11.276	3.158	6.710

Cortaderia selloana (K1) translocated B, V, Cr, Mn, Co, Ni, Cu, Zn, As, Sr, Cd, Sn, Sb, Ba, Hg, Pb, Al, Fe, Ca, K, Mg, Na, P and Si while *Cortaderia selloana* (K2) translocated B, V, Mn, As, Se, Sr, Sn, Sb, Ba, Pb, Ca, K, Mg, and Si from the roots to the shoots. The difference in translocation between K1 and K2 is the plant development level. K1 was more developed in terms of growth as compared to K2. *Populus alba* translocated B, V, Mn, Co, Ni, Zn, As, Se, Sn, Sb, Hg, Pb, Fe, K, Mg, P and Si from the roots to the shoots. This was shown by the TF value of the latter elements which was greater than1 (>1), indicating the plants ability to translocated certain elements. Since both species showed higher translocation factor in potentially toxic metals such as Cr, Mn, Co, Ni, Zn, As, Pb, Fe and Mg, this implied that they both have the potential to phytoextract latter metals. Although, *Cortaderia selloana* showed a higher translocation factor in all studied chemical species, except for Se, this indicated that this plant species has a greater potential to be used in phytoextraction.

Table 3.6: Bioconcentration factor (BCF) of toxic chemical species in *Cortaderia selloana* and *Populus alba*.

Cations	***Cortaderia selloana***				***Populus alba***		
	Leaves K1.1	**Roots K1.2**	**Leaves K2.1**	**Roots K2.2**	**Leaves 3.1**	**Stem 3.2**	**Roots 3.3**
B	3.93	0.92	3.54	1.03	36.27	7.74	12.76
V	0.04	0.01	0.05	0.03	0.13	0.04	0.06
Cr	0.38	0.06	0.36	0.56	0.26	0.25	0.36
Mn	1.48	0.11	1.27	0.50	6.45	1.92	3.96
Co	0.20	0.17	0.07	0.40	13.03	2.03	3.20
Ni	0.59	0.20	0.24	0.49	8.02	1.48	3.83
Cu	0.45	0.13	0.20	0.33	1.01	1.65	2.79
Zn	1.28	0.42	0.34	0.58	14.03	9.43	6.23
As	0.02	0.00	0.02	0.02	0.09	0.04	0.06
Se	0.05	0.06	0.05	0.02	0.07	0.03	0.05
Sr	1.11	0.61	0.90	0.72	1.98	1.87	11.07
Cd	0.56	0.36	0.16	0.31	31.59	37.27	24.75
Sn	0.01	0.01	0.01	0.01	0.01	BDL	0.01
Sb	0.02	0.01	0.02	0.02	0.02	6.18	0.06
Ba	0.18	0.13	0.18	0.14	0.46	0.28	0.87
Hg	0.05	0.05	0.05	0.06	0.14	0.14	0.17
Pb	0.04	0.00	0.02	0.02	0.18	0.49	0.08
Al	0.03	0.01	0.01	0.04	0.20	0.09	0.64
Fe	0.03	0.01	0.02	0.03	0.09	0.03	0.05
Ca	1.09	0.14	0.77	0.34	3.66	2.25	10.48
K	57.20	8.58	32.21	24.37	115.17	31.87	26.38
Mg	1.71	0.20	0.59	0.44	3.27	1.02	1.65
Na	0.07	0.02	0.01	0.05	0.79	0.59	6.06
P	8.79	2.00	4.40	8.42	53.51	23.66	32.34
Si	1.22	0.11	0.79	0.25	0.85	0.10	0.14

The bioconcentration factor of B, Mn, Zn, Sr, Ca, K, Mg, P and Si was found to be greater than 1 in the leaves of *Cortaderia selloana* (K1). The roots of *Cortaderia selloana* (K1) had BCF greater than 1 for P and K. Similar pattern was observed for *Cortaderia selloana* (K2) which was collected 50 m away from K1 on Mooifontein2 except that K2 had higher BCF for B, Mn, K and P in the leaves, and B, K and P in the roots. The concentrations of B, Mn, K and P at the sampling point (K2) are 1.23 mg/kg, 35.98 mg/kg, 133.08 mg/kg, and 40 mg/kg respectively. However, the concentration of the same elements (B, Mn, K, P) in mine tailings at approximately 50 m away from K2 are 2.34 mg/kg, 133.47 mg/kg, 210.4 mg/kg, and 50.9 mg/kg respectively. There is difference in concentration from the sampling point K2 and 50 m away from it, this could be explained by the accumulation of this elements into plant tissues. Furthermore, both *Cortaderia selloana* plant samples had BCF>10 of K in the leaves and the roots, except in the roots of sample K1. The *Populus alba* on the other had showed BCF of greater than one in B, Mn, Co, Ni, Cu, Zn, Sr, Cd, K, P and Mg within the leave tissues. Furthermore, in the stem tissues the BCF greater than 1 was found in B, Mn, Co, Cu, Ni, Zn, Sr, Cd, Sb, P, Mg, K and Ca, while in the roots it was Mn, Ni, Cu, Zn, Mg and Na. The *Populus alba* showed BCF greater than 10 in B, Co, Zn, Cd, K, Ca, Sr and P across different plant tissues. With higher BCF in the leaves for most of the chemical species in *Cortaderia selloana and Populus alba*, indicated that both plants species have the potential to be used in phytoremediation. *Populus alba* bioaccumulated more chemical species in the leaves, stem and roots as compared to *Cortaderia selloana* species. Consequently, *Populus alba* has greater potential to be used in phytoremediation of Gold mine tailings compared to *Cortaderia selloana*.

3.5 Summary

From this chapter, the physicochemical characteristics of abandoned gold mine tailings from Crown mine in Johannesburg and their acidic leachates were successfully evaluated. Moreover, the capabilities of *Cortaderia selloana* and *Populus alba* to phytoextract the inorganic chemical species were evaluated. The analysis revealed that the pH of the mine tailings ranges from 6.21 to 6.84. The elemental composition revealed the dominance of Ca, Fe, Al, Mg, Si and Na in the mine tailings. The pH, EC and TDS of the leachates were found to be ranging from 3.31 to 5.13, 3887 to 5517 mS/cm and 1903 to 2704 mg/L respectively. Leachates were found to be dominated by chemical species such as Fe, Ca, K, Na, Mg, Al, Si, and Mn as the major elements. Trace elements detected in both tailings and leachates includes Se, Sb, Sn, Cd, Cu, Co, Pb, Sr, B, and V. The composition of the leachates and mine tailings showed that they both have the potential toxic effects on the natural environment. The evaluated plant species are *Cortaderia selloana* and *Populus alba,* have the potential accumulate inorganic chemical species in their leaves compared other parts of the plants. Translocation factors confirmed that both plants species has the ability to translocate chemical species from roots to other parts of the plants. Bioconcentration factor indicated that *Cortaderia selloana* can potentially be used for phytoextraction of B, Mn, Zn, Sr, Ca, Mg, P, and Si, and is a hyperaccumulator of K. Similarly, bioconcentration factor revealed that *Populus alba* can potentially be used for phytoextraction of Mn, Ni, Cu, Sb, Na and Mg, and is a hyperaccumulator of B, Co, Zn, Ca, Cd, K, P, and Sr. Therefore, based on these findings, both plant species can be used for phytoremediation gold mine tailings. This study further recommends the evaluation of using both species in treatment of acidic leachates owing to their ability to phytoextract chemical species from mine tailings. Moreover, the study recommends evaluating the prospect of using *Populus alba* in phytomining of metal species owing to its ability hyperaccumulate various chemical species.

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Chapter 4: Physicochemical properties of acid mine water from decant points in eMalahleni, Mpumalanga and contaminants retention potential of selected plants and sediments in natural wetlands.

Abstract

Acid mine drainage is continuously discharging from Mpumalanga, eMalahleni abandoned coal mines to the environment and flows into the nearby streams and wetlands and finally enter the Olifants River Catchment. This chapter aimed at evaluating the physicochemical characteristics of the acidic mine water discharging from the coal mine shafts in eMalahleni, Mpumalanga and further assess the inorganic chemical species retention capabilities of sediments and plant species within the stream wetlands. A total of 28 water samples, 7 plant species and 7 sediment samples were collected from the mine shaft water discharging points, mine water ponds, upstream and downstream of the wetlands. A total of four flooded mine shafts were identified from Blesboklaagte mine, Transvaal and Delagoa Bay Brugspruit Colliery and Douglas colliery. The pH, redox potential (Eh), electrical conductivity (EC), total dissolved solids (TDS), salinity and dissolved oxygen (DO) were measured in the field. The inorganic metal species in water, sediments and plant samples were analysed using Inductively Coupled Plasma-Mass Spectrometry, and anions were determined by Ion Chromatography. The physicochemical characteristics such as pH, EC, TDS, Eh, DO and Salinity were found to be ranging from 2.53 to 3.6, 1066 to 2285 µS/cm, 610 to 5230 mg/L, 194 to 256.8 mV, 2.94 to 8.24 mg/L and 0.82 to 6.09 psu, respectively. The concentration of SO_4^{2-}, Cl^-, NO_3^{2-}, and F^- were found to be ranging from 992.90 to 12580.38, 19.63 to 160.61, 1.77 to 23.56, and 4.76 to 14.95 mg/L, respectively. The dominant inorganic chemical species in water were found to be Ca (65 to 467 mg/L), K (1.3 to 34.6 mg/L), Mg (31.2 to 190.7 mg/L), Na (5.7 to 1488 mg/L), Si (10.9 to 55.8 mg/L), Al (14.54 to 89.21 mg/L), Fe (0.55 to 234.9 mg/L), Zn (0.65 to 4.19 mg/L) and Mn (6.10 to 42.27 mg/L). The sediments collected along the streams showed higher concentration of Fe (16326 to 286600 mg/kg), Ca (234.60 to 2098 mg/kg), Al (3570 to 18442 mg/kg), K (180.9 to 1695.2 mg/kg), Mg (63.38 to 610.8 mg/kg), Na (81.30 to 4354 mg/kg), P (88.80 to 3780 mg/kg), Si (127.90 to 440.80 mg/kg), Zn (9.43 to 6182.69 mg/kg), Mn (30.81 to 142.61 mg/kg) and V (38.78 to 2603.12 mg/kg). This suggests that sediments were reservoirs of the potentially toxic elements. The concentration of metals in plants tissues ranged as follows: Cr (2,7 to

56,5 mg/kg), Mn (20,7 to 807,8 mg/kg), Co (1,7 to 20,5 mg/kg), Ni (3,7 to 40,3 mg/kg), Cu (4,4 to 27,1 mg/kg), Zn (24,4 to 492,0 mg/kg), As (0,2 to 3,4 mg/kg), Cd (50,2 to 1945,8 mg/kg), Pb (0,3 to 10,3 mg/kg), Al (75,7 to 2342,0 mg/kg), Fe (714,8 to 49800 mg/kg) and Mg (379,6 to 2108,0 mg/kg). Among the plant species collected, *Cyperus esculentus* and *Juncus lomatophyllus* proved to be having hyperaccumulation potential for Cd, Na, Mg and K. This was confirmed by the bioconcentration factor which was found to be greater than one. Therefore, both plant species showed higher accumulation in the leaves than in the roots. *Cyperus esculentus* and *Juncus lomatophyllus* has greater potential to be used in phytoremediation of mine water.

Keywords: *Abandoned Coal mine, mine water, Inorganic contaminants, Retention mechanisms, natural wetland, bioconcentration factor, translocation factor*

4.1 Introduction

Mining of coal plays a crucial role in the country's economy, with about 93% of the country's electricity generated by coal-fired stations (Eberhard, 2011). Despite the economic benefits of coal mining in eMalahleni, there are several environmental problems associated with mining. This is due to large amounts of toxic waste (acids, salts, metals) and high volumes of contaminated water produced and released into the environment, which destroys biodiversity (DWS, 2017). Mining activities has taken a larger surface area in eMalahleni and has further contaminated the land through solid mine waste and mine water disposal into the environment. The Centre for Environmental Rights (CER) indicated that pollution of water sources from the collieries in Mpumalanga was outstandingly bad and mining companies had failed to live up to their water use licence obligations (Mckay, 2019). Studies have indicated that mining disturbance could alter water flow-paths and increase runoff, erosion, nutrient leaching and drainage, subsurface void space, and baseflow (Bonta, 2000; Negley and Eshleman, 2006; Feng *et al*., 2019).

Acid mine drainage is the major cause for water pollution problems in Emalahleni (Bell *et al*., 2001). The nature and rate of release of acid mine drainage is controlled by various chemical and biological reactions. Acid mine drainage can pose a serious threat to the environment, due to its containment of large amounts of toxic waste (acids, salts, metals), which can potentially destroy biodiversity (Bell *et al.,* 2001; DWS, 2017). WWF-SA (2011) reported that in the year 2004 an estimate of 50 000 m^3 of contaminated mine water was discharged into the Olifants river per day, with an additional of 64 000 m^3 discharged from the abandoned collieries. This negatively affected freshwater ecosystems, deteriorated water quality in the Olifants River Catchment, hence affecting water supply in eMalahleni. In view of this, Olifants River catchment was regarded as one of the most contaminated rivers in Southern Africa (CSIR, 2011).

In the previous years Eskom was extracting water from Olifants river for power generation. However, due to the deterioration of the water quality in the catchment, such water can no longer be used in coal-fired power stations (CER, 2016). CER (2016) reported that throughout the years fish have been dying in the Loskop Dam of the Olifants River catchment. The scientists concluded that this could be due to acid mine drainage from the collieries in eMalahleni. Besides, water pollution acid mine drainage also has a negative impact on the soils and vegetation. Most plants fail to tolerate the acidity in water and/or soil because high concentration of hydrogen ions deactivates the enzyme systems and restrict transpiration and root uptake of mineral salts and water (Bradshaw *et al*., 1982). Furthermore, high concentrations of different toxic metals from the soil translocated into plant tissues can inhibit plant growth.

Natural wetlands are well known to be efficient at removing pollutants from contaminated water by creating reducing conditions which cause reduction of sulphate ions to sulphide (Humphries *et al*., 2017). Oberholster et al. (2016) reported the performance of Grootspruit wetland in eMalahleni, in their study they reported reduction in the concentrations of Mn (from 125 to 35 mg/L), Fe (from 0.3 to 0.02 mg/L), Cl (from 118 to 50 mg/l) and As (1.3 to 0.2 µg/L) and further increase in pH (from 3.89 to 7.4) at upstream to downstream. It was then reported that filtration, suspension of pollutants as well as biologically mediated processes were responsible for the decrease in concentrations of pollutants in the wetland. Bello *et al*. (2018) studied the performance of *Phragmites australis* in the uptake of Cd, Ni and Pb in hydrophonic system and they found that the plant species can bioaccumulate and translocate all studied metals. The bioconcentration factor for Cd was 1.14, for Ni it was 0.86 while Pb it was reported to be 1.6, the translocation factor for Cd, Ni, Pb was 0.43, 0.36, 0.37, respectively. Plants with high bioconcentration factor (>1) and low translocation factor (<1) are suitable for phystabilization whereas plants with high bioconcentration and translocation can be used for phytoextraction of toxic metals and/or pollutants (Nouri *et al*., 2011; Bello *et al*., 2018)

To date most studies conducted in Mpumalanga region have not looked into the performance of chemical species retention by natural wetlands. Most of the studies have assessed the metal accumulation capacities of the plant species under controlled conditions at a laboratory scale (Novhe *et al.*, 2016; Kiiskila *et al*., 2017; Dube *et al*., 2019). Blesbokspruit and Brugspruit wetlands in the study area are receiving acid mine drainage from the discharging points in abandoned colliery. The plant species dominating in Blesbokspruit and Brugspruit wetlands differs from place to place, however the common native plant species in all areas are *Juncus effussus, Cyperus esculentus and Phragmites mauritianus*. To contribute towards development of sustainable mine water management solutions in South Africa, more native aquatic plant species should be identified and assessed for their potential in accumulation of potentially toxic chemical species under field conditions. The advantages of using native plant species include not invasive, they survive well with other existing species without outcompeting them, they do not interrupt with the hydrological processes and they adapt well. Therefore, detailed baseline information on the accumulation properties of aquatic plants can help in the selection of appropriate plant species for wetland phytoremediation systems (Eid and Shaltout, 2014). This study is aimed at characterizing acid mine drainage, sediments and plant species, and further investigated retention capabilities of inorganic contaminants by sediments and six identified aquatic plant species (*Cyperus esculentus*, *Phragmites mauritianus, Juncus effussus, Juncus lomatophyllus, Typha capensis and Cynodon dactylon).* This study was conducted at Mpumalanga, eMalahleni where mine water/acid mine drainage was discharging from flooded underground mine shafts and flows into the nearby wetland streams.

4.2. Description of Study area

The study was conducted in eMalahleni formerly known as Witbank situated in Mpumalanga Province, South Africa. The site is located in the Nkangala District and lies between the GPS coordinates of 25° 52' 22.02'' S and 29° 15' 19.16'' E as indicated in Figure 4.1, and 1572m above sea level (Sergienko, 2015). The area receives average long-term rainfall of between 600 and 1100 mm (SAWS, 2016). Furthermore, the area experiences cold winters with more precipitation, and the average temperature ranges between 4 ^{o}C to 16 ^{o}C, while the summers are warm with temperatures ranging between 16 ^{o}C and 26 ^{o}C (Climate-Data, 2021). The province has over 4000 wetlands and five major catchment areas including headwaters from Vaal, Olifants, Nkomati, Crocodile and Usutu rivers (CER, 2016). Despite several resources of water, the region can be described as water-stressed due to increasing population, climate change resulting in a decrease of annual rainfall and high levels of water contamination. The area is dominated by active and abandoned collieries, with most of the wastewater from the mines discharging into the Olifants River.

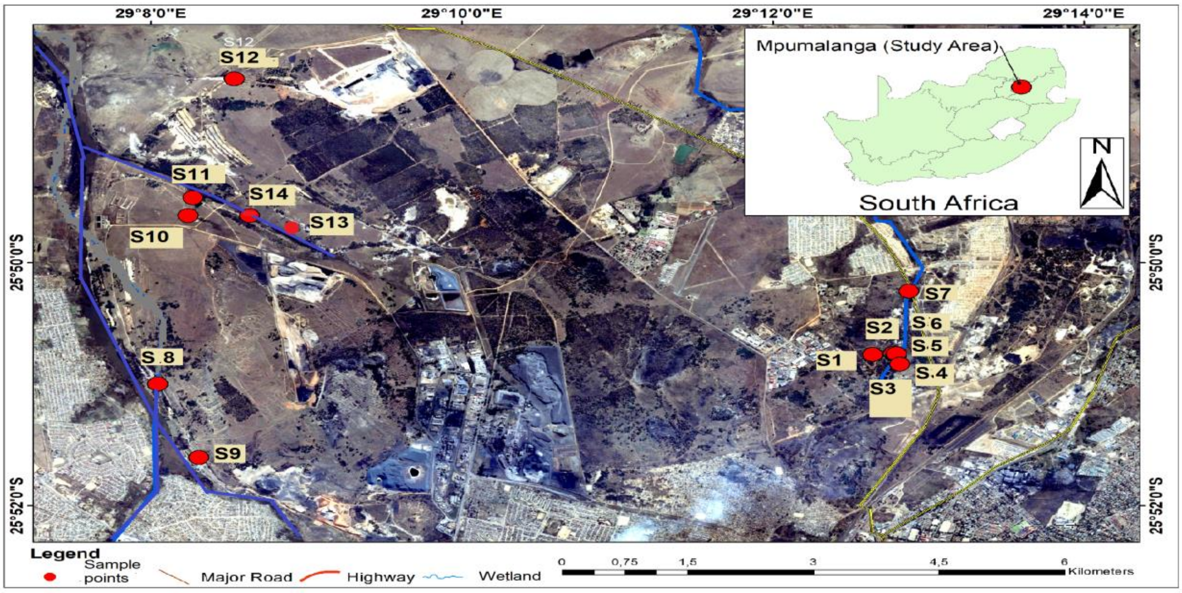

Figure 4.1: Study area and sampling points.

The general geology of the study area consists of weathered regolith that is underlined by alternating layers of siltstone, sandstone, and carbonaceous shale of the Karoo Basin (Cairncross and McCarthy, 2008; Gomo and Vermeulen, 2014). The main Karoo Basin overlies the central and eastern parts of South Africa. Dolerite dykes and sill intrusions are also common features throughout the study area (Johnson *et al.*, 2006). Coal seams occur between alternating layered sedimentary rocks (Gomo and Vermeulen, 2014). Pyrite is a common sulphide mineral in the Witbank coal (Azzie, 2002; Pinetown and Boer, 2006) and the associated problems of AMD in the environment are known worldwide. Studies have reported the existence of acid-neutralizing minerals such as calcite and dolomite that occurs together with pyrite within the Witbank coal seams (Van Vuuren and Cole, 1979, Gaigher, 1980, Van der Spuy and Willis, 1991, Usher *et al.*, 2001, Azzie, 2002, Pinetown and Boer, 2006).

4.3 Materials and methods

4.3.1 Sediments, water, and plant sampling

Table 4.1 shows the GPS coordinates, the name of the location and a brief description of where the samples were collected. Sediments, water, and plant species were collected from different points as indicated in Table 4.1. Sampling sites were selected randomly considering the discharge points, upstream and downstream of the wetland as well as mine water retention ponds.

Table 4.1: GPS coordinates, location, and a brief description of the sampling points.

Sample ID	Coordinates	Location	Description
S1, S1a and S1b, and T1a and T1b	25°50'45.3" S 29°12'3835" E	Blesboklaagte	Flooded underground mine shaft
S2	25°50'44.8" S 29°12'46.4" E	Blesboklaagte	Surface runoff
S3	25°50'45.6" S 29°12'47.3" E	Blesboklaagte	Outflow from the pond
S4 and T4	25°50'45.4" S 29°12'47.7" E	Blesboklaagte	Upstream of the wetland
S5	25°50'44.9" S 29°12'47.7" E	Blesboklaagte	Inflow into the wetland
S6	25°50'50.1" S 29°12'48.7" E	Blesboklaagte	Retention pond
S7 and T7	25°50'14.1" S 29°12'52.5" E	Blesboklaagte	Downstream of the wetland
S8	25°50'59.8" S 29°08'02.5" E	Brugspruit	Flooded shaft
S9 and T9	25°51'36" S 29°08'184" E	Brugspruit	Flooded shaft
S10	25°49'36.8" S 29°08'14.2" E	Douglas 1	Entry to the pond
S11	25°49'27.9" S 29°08'16" E	Douglas 1	Outflow from the pond
S12	25°48'29.2" S 29°08'32.1" E	Douglas 1	Surface runoff from the flooded shaft
S13	25°49'41.6" S 29°08'46.1" E	Douglas 1	In the midst of the wetland
S14 and T14	25°49'41.6" S 29°08'49.1" E	Douglas 2	Downstream of the wetland

Figure 4.2 shows the flooded mine shafts and water seepages from underground. Samples were collected from abandoned flooded mine shaft, mine water retention ponds, wetlands and along the stream in Blesboklaagte, Brugspruit and Douglas. A total of 28 water samples were collected using HDPE plastic bottles which were pre-cleaned with distilled water and rinsed with 3 M nitric acid (Tutu *et al.*, 2008; RoyChowdhury *et al.*, 2015). Water samples were collected in pairs with one designated for metal cations and the other for anions. Samples for cation analysis were acidified with a drop of 3M HNO_3. Physicochemical parameters such as pH, EC, Eh, DO, TDS and salinity were determined in the field using pre-calibrated Thermo Scientific Orion Star A324 pH multi-meter (Waltham, Massachusetts). Water samples were preserved in a cooler box with ice cubes and transported to the laboratory and stored at <4 ^{o}C till analysis.

Figure 4.2: Flooded mine shafts and water seepages from underground.

Figure 4.3 shows the identified plant species growing around discharge points, ponds, streams and wetland. A total of 7 plant samples, with 2 plant samples of *Cyperus esculentus*, and 1 sample of *Phragmites mauritianus, Juncus effussus, Juncus lomatophyllus, Typha capensis* and *Cynodon dactylon.* Plants were uprooted using garden spade together with sediments and stored in sealable plastic bags separately. Plants were selected based on their survivability in harsh conditions.

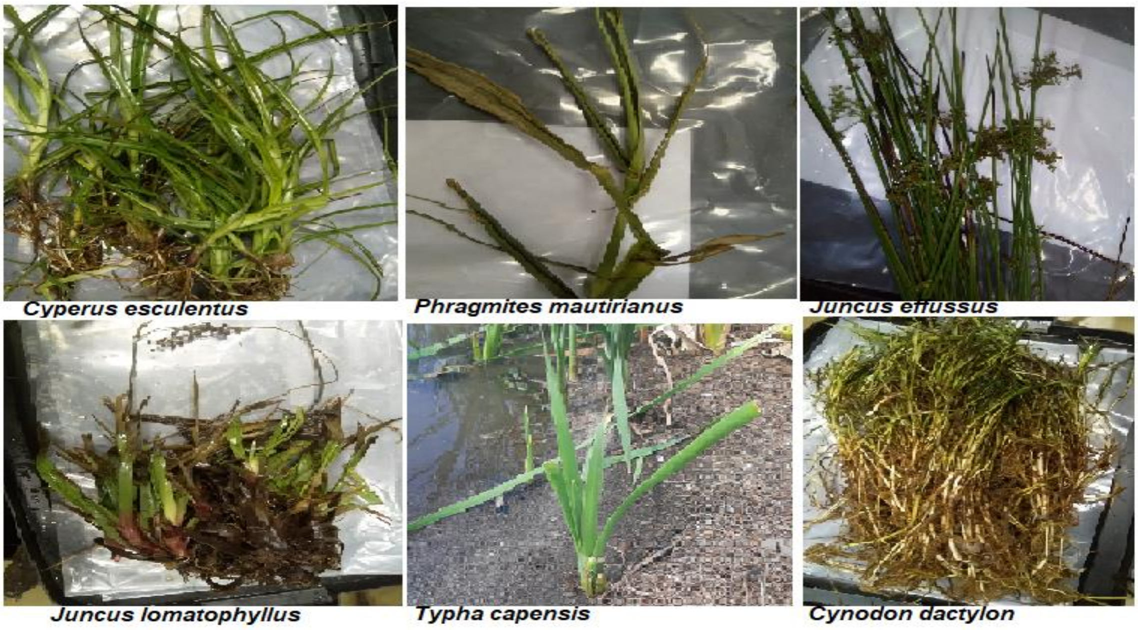

Figure 4.3: Identified plant species

4.3.2 Analysis of sediments, mine water, and plant species

Before analysis, the sediments were air-dried, then milled into homogeneous powder using Retsch RS 200 Vibratory Disc Mill (Duesseldorf, Germany). Sediments were then digested using aqua regia method following the procedure described by Joseph *et al.* (2017). Briefly, A volume of 15 mL of concentrated HNO_3 and 45 mL of concentrated HCl was added to 5 g of milled sediments for 90 to 120 mins. After digestion, the beaker was allowed to cool to room temperature and the contents were transferred into 100 mL volumetric flask and filled up to the mark with deionised water. Volumetric flask was shaken vigorously and allow to settle for 2 hours before filtering. For the analysis of metals in plants, plant samples were separated into different parts (roots, leaves and stem) and washed with deionized water to remove excess soil. Washed samples were then air-dried for a day to remove excess moisture and then oven-dried at 80 ^{o}C for 4 days. Dried plant samples were ground into powder using a coffee bean grinder (Sunbeam, Chicago, USA). This was followed by digestion using the aqua-regia method. The metal content in both samples was analysed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Agilent 7900, Santa Clara, Califonia), at the central analytical laboratory of Stellenbosch University. The anions were determined using Ion chromatography (Metrohom, 850 professional IC, Herisau, Switzerland).

4.3.3 Metal accumulation potential

The plants metal accumulation potential was assessed by calculating the bioconcentration factor and translocation factor. The bioconcentration factor (BCF) and translocation factor (TF) of different metals from sediments to plants was calculated based on dry weight of plant samples. The following equations were used:

$$BCF = \frac{Cplant\ organ}{Cmine\ tailings} \qquad 4.1$$

$$TF = \frac{Cshoot}{Croots} \qquad 4.2$$

C - Mean concentration of plant tissues/ mine tailings

Plant organ- leaves/stem/roots

4.4. Results and discussions

4.4.1 Physicochemical characterization of mine water.

The geochemical characteristics of the water samples collected from the discharge points of eMalahleni collieries and different sources including retention ponds, steams and wetland water are summarized in Table 4.2. The values of the physicochemical parameters of the water samples were compared with the wastewater discharge regulation stipulated by the DWAF of 1999.

Table 4.2: Physicochemical parameters of mine water samples

Physicochemical parameters	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	Wastewater limit (DWAF)
pH	3.3	2.76	2.69	2.71	2.74	2.75	2.95	2.53	3.38	3.6	3.37	2.82	3.01	3.01	5.5-9.5
EC µs/cm	1863	2594	2704	2660	2605	2617	3110	5584	1066	1238	1906	1532	3349	3248	700-1500
TDS mg/L	910	1270	1330	1300	1280	1280	1520	2740	5230	610	930	750	1640	1590	25
Eh Mv	214	245.3	250.3	249.1	247.6	247.3	234.9	256.8	210.8	194	208.8	239	226.6	229.3	
DO mg/L	3.65	5.96	8.15	7.73	7.87	7.68	7.67	7.68	2.94	7.77	7.57	8.24	7.12	7.42	
Salinity psu	1.00	1.39	1.45	1.43	1.39	1.40	1.67	3.06	6.09	0.66	1.02	0.82	1.79	1.74	
Cl^- mg/L	60.37	81.87	81.01	66.96	77.72	62.39	160.61	-	158.77	-	-	-	16.63	26.06	0.25
$SO4^{2-}$ mg/L	992.90	1190.24	1320.52	1321.24	1233.42	1310.07	1808.33	9584.45	12580.38	1435.84	1888.17	1691.78	5218.30	6840.98	
Cr ug/L	7.8	18.8	17.4	16.6	20.5	11.9	36.6	43.0	4.0	2.5	11.2	4.7	31.4	33.7	0.05
Cu ug/L	6.8	28.6	13.6	25.6	45.1	17.7	30.9	152.8	17.7	82.3	62.7	27.7	69.8	71.2	0.01
As ug/L	2.63	5.50	6.63	7.33	6.04	5.72	17.93	43.17	2.28	14.40	13.54	5.64	35.05	35.56	0.02
Cd ug/L	3.77	3.94	3.32	5.17	3.92	3.79	7.51	31.17	8.16	2.60	4.17	2.33	9.81	9.39	0.005
Pb ug/L	3.8	3.5	11.9	12.4	7.2	14.7	3.0	1.9	0.9	7.3	6.9	1.7	1.7	1.2	0.01
Co mg/L	0.41	0.50	0.57	0.58	0.55	0.59	0.86	3.65	0.49	0.29	0.56	0.70	1.51	1.49	
Ni mg/L	0.53	0.55	0.68	0.67	0.61	0.70	0.79	6.90	0.70	0.24	0.49	0.78	1.77	1.72	
Ca mg/L	124	136	139	141	144	139	199	208	467	81	129	65	210	206	
K mg/L	5.1	4.9	6.8	6.7	5.9	6.5	8.9	**BDL*	34.6	**BDL*	1.3	2.4	5.1	4.8	
Mg mg/L	60.0	59.1	71.4	71.7	66.8	71.5	98.7	190.7	212.6	31.2	55.5	38.5	124.5	121.7	
Na mg/L	63.4	93.4	78.8	77.5	93.2	75.8	132.8	5.6	1488.0	30.3	38.6	5.7	61.8	58.2	
Si mg/L	49.3	39.0	55.3	55.4	46.6	55.8	30.6	36.0	39.6	10.9	15.9	11.4	19.7	18.8	
Al mg/L	50.49	66.14	74.52	74.27	72.35	72.37	89.21	214.8	14.54	31.91	54.91	31.87	81.79	82.77	
Fe mg/L	55.5	40.26	30.38	30.73	37.54	30.93	20.39	234.9	110.4	0.55	0.97	34.79	28.95	22.39	0.3
Zn mg/L	1.919	1.803	1.914	1.903	1.931	2.092	2.408	14.94	2.74	0.65	1.29	2.047	4.185	4.085	0.1
Mn mg/L	9.029	15.88	12.24	12.43	15.36	12.05	21.07	79.11	15.69	6.096	12.04	10.66	42.27	41.7	0.1

As observed in Table 4.2 all water samples are acidic with their pH ranging from 2.53 to 3.6. The acidic pH was accompanied by positive redox potential which was ranging from 194 mV to 256.8 mV (Table 4.2). Similar results of AMD were reported by Fosso-kankeu *et al.*, (2017) in Mpumalanga province. Baruah *et al.* (2006) explained that the lowering of pH is due to the production of sulphuric acid by oxidation of pyritic sulphur and other sulphides present in coal and accompanying strata. From the discharging point (S1) to surface runoff (S2 and S3) the pH was decreasing, this may be due to further oxidation processes taking place and possible cascading of water as it flows through the undulating surface. There was an increase in pH as the water flow inside the wetland (S4 and S5, as well as in the pond) and it continued increasing downstream of the wetland (S7). Skousen et al. (2000) indicated under anaerobic conditions, sulphate-reducing bacteria produces iron mono and di-sulphides while reducing the sulphate present in the AMD water and also increases the pH of water. Although the pH was increasing, it remained acidic, and this can destroy the aquatic biodiversity and contaminate limited freshwater resources. Electrical conductivity (EC) ranged from 1066 to 3349 µS/cm and these results falls within the same range observed by Fosso-kankeu *et al.* (2017), while TDS ranged from 610 to 5230 mg/L. The high values of EC and TDS, of water samples indicated higher dissolution of salts and mineral compounds into ions (Dutta *et al.*, 2017; Mohanty *et al*., 2018). The obtained mean values for pH and EC (2.9 and 2.6 mS/cm) are in the same range as the results obtained by Dube *et al.* (2019). The lowest pH (2.53) and highest EC (5584 µs/cm) were recorded at a discharge point (S8) in Transvaal and Delagoa colliery as illustrated in Table 4.1. The concentrations of Fe were observed to be higher with values 55.5 mg/L, 234.9 mg/L and 110.4 mg/L in the discharging points S1, S8 and S9, respectively, as compared to other sampling points and this concurred with low pH and high EC. This implied that the acidification probably resulted from the oxidation of pyritic particles, and similar results were reported in Fosso-Kankeu *et al.* (2015) and Fosso-Kankeu *et al.* (2017). The DO values ranged from 2.94 to 8.24 mg/L, with 2.94 mg/L and 3.36 being the lowest values from the discharging points S9 and S1 respectively. The highest values of DO we observed from sample S3 (8.24 mg/L) in the wetland and S12 (8.13 mg/L) a runoff from a discharging shaft. Oxygen enhances oxidation of sulphide minerals, and as a result it reduces the pH. Consequently, high values of DO influences low values of pH (Chou *et al.*., 2018) and the results from the present study confirmed this phenomenon. The inverse relationship between DO and pH was clearly observed in the discharge points such as S1 (pH 3.30, DO 3.65 mg/L), S2 (pH 2.76, DO 5.96 mg/L), S8 (pH 2.53, DO 7.68 mg/L) and S9 (pH 3.38, DO 2.94 mg/L), with S9 having the lowest DO value (2.94) and the pH value of 3.38 (Table 4.2). Dissolved oxygen can affect the rate of oxidation and reduction of metals, consequently this can influence desorption and adsorption of metals. The concentrations of chloride and sulphates were found to be ranging from 16.63 to 158.77 and 992.90 to 12 580.38 mg/L, respectively. The mean values for sulphates (3458.3 mg/L) and chloride (4.3 mg/L) reported in this present study were found to be higher than the mean values of sulphates (1006.4 mg/L) and chloride (0.9 mg/L) reported by Dube *et al.* (2019), which was conducted in the same study area. The possible sources of sulphates are dissolution of sulphide rich minerals. The dominant toxic inorganic metal species were found to be Cu, Cr, Cd, As, Fe, Pb, Mn, Al, and Zn. This implied that the underlying geology is igneous and metamorphic rocks, hosting metallic minerals. It can be noted that S8 and S13 had the highest metal concentration, while S1 and S10 had the least metal concentrations. Sample point S1 and S8 are old mine shafts discharging mine water, S10 is the inlet to the pond while S13 is in the midst of a wetland. The low metal concentration at S10 could be due to processes such as adsorption and precipitation along the the pond. All these metal species were found to be exceeding the general wastewater discharge limit as stipulated by the South African Department of Water Affairs (DWAF, 1999). Figure 4.4 shows the iron precipitation observed in the field at Blesboklaagte.

Figure 4.4: Orange/red precipitates observed in the field.

At the highest pH (S10) there was a significant drop in Fe concentration and oxidation of Fe, leading to precipitation could have attributed to this effect, similar results were observed in Fosso-Kankeu *et al.* (2017). The orange/red precipitates in Figure 4.4 were observed in the field as evidence of precipitated iron (ferric iron). and the high concentration of toxic metals may be poisonous for aquatic flora, fauna, and nearby wild organisms (Jain and Das, 2017). Furthermore, this will contaminate the neighbouring water resources and cause acidification of the surrounding sediments. Higher concentrations of these metal species may cause several health impacts on human beings such as cancer, cardiovascular diseases, abdominal pains, diarrhoea, skin rash and kidney failure (Moeng, 2019).

4.4.2 Elemental concentrations in sediments

The elemental composition of sediments collected from different sites are present below in Table 4.3.

Table 4.3: Elemental composition of sediments

Cations (mg/kg)	T1 a	T1 b	T4	T7	T9	T10b	T14
Cr	70.37	65.05	26.55	92.70	28.81	81.09	76.39
Mn	74.45	142.61	32.50	51.54	73.20	30.81	128.54
Co	7.45	114.83	1.39	5.34	7.96	2.12	6.65
Ni	16.47	172.91	3.80	11.70	16.78	3.00	15.68
Cu	56.35	137.86	9.74	39.10	20.70	12.76	40.62
Zn	1021.58	6182.69	10.25	56.30	203.55	9.43	50.63
As	13.54	14.12	1.80	4.31	37.33	6.35	15.12
Cd	3.98	21.49	0.03	0.40	1.03	0.05	0.23
Pb	38.97	73.01	12.98	24.81	3.62	5.18	29.56
Al	13556	18442	4906	15364	11296	3570	15410
Fe	286600	269400	16326	22500	361600	25040	78580
Ca	444	1670.20	234.60	260.60	464.40	517.40	2098
K	180.9	240.2	448.8	685	1675.6	148.48	1695.2
Mg	186.88	329.4	107.44	280.6	610.8	63.38	319
Na	87.74	206.20	108.78	278.40	4354	81.30	250.60
P	3680	2674	51.30	1423.80	3780	88.80	484
Si	420.60	440.80	343.00	436.40	290.40	127.92	371.20

The results in Table 4.3 shows that sediments have higher concentrations of Fe, Ca, Al, K, Mg, Na, P, Si, Zn, Mn and V as compared to water samples (Table 4.2). This shows that sediments serve as reservoir for all these chemical species up taking them from the contaminated water. The sediments from the discharge points (T1a, T1b and T9) had higher concentrations of potentially toxic metals such as Fe, Zn, As, Cu, Co, Mn, and Ni. A similar trend was observed in water samples, and this is expected since these sample points are located at the source of pollutants. There is a significant decrease of concentration in all studied elements in water samples, except for Cr, K, and Na from the discharging point and surface runoff (S1 to S6) in Blesboklaagte collieries downstream of the wetland (S7) within that area. The same trend of decreasing concentration in Co, Ni, Zn, As, Cd, Mg, P, Fe, and Na from the discharging points to downstream of the wetland, has also been observed from samples collected at Douglas colliery (T9, T10b, and T14). Consequently, the inverse trend was observed in water samples, whereby metal concentration increases in sediments and decreases in water samples. This implies that the sediments could be responsible for retaining the potentially toxic metals through adsorption. Fosso-kankeu *et al*. (2017) observed similar trend of decreasing metal concentration in water as it flows downstream in a study conducted in Mpumalanga Highveld coalfield and stated that this could be an indication of adsorption of metals in the sediments along the stream.

4.4.3 Elemental concentrations in different plant species

A total of six native plant species (*Phragmites mauritianus, Cyperus esculentus, Typha capensis*, *Juncus lomatophyllus* and *Cynodon dactylon*) were identified and collected around discharge points, retention ponds, streams, and wetlands within the study area. The concentration of various elements in the tissues of identified species of plants are presented in Table 4.4.

Table 4.4: Concentration of chemical species in different parts of the studied plant species.

Cations (mg/kg)	*Cyperus Esculentus* (S1a)		*Phragmites mauritianus* (S1b)		*Cyperus Esculentus* (S4)		*Juncus effussus L.* (S7)		*Cynodon Dactylon* (S9)		*Juncus lomatophyllus* (S10)		*Typha Capensis* (S14)	
	Leaves	**Roots**	**Leaves**	**Roots**	**Leaves**	**Roots**	**Leaves**	**Roots**	**Leaves**	**Roots**	**Leaves**	**Roots**	**Leaves**	**Roots**
Cr	4.1	7.1	10.2	8.0	34.3	32.6	3.9	25.6	2.7	4.5	5.2	56.5	8.9	6.4
Mn	116.5	22.9	53.6	56.8	149.1	118.1	213.1	86.5	34.6	20.7	690.6	108.4	807.8	342.1
Co	2.8	4.9	2.6	20.5	3.7	5.6	4.3	8.5	1.7	3.5	4.3	9.9	4.1	7.5
Ni	7.2	8.3	7.6	40.3	20.2	13.0	10.0	11.4	3.7	7.1	7.8	7.9	7.5	7.9
Cu	12.3	13.9	4.5	22.1	13.0	21.2	11.1	14.2	4.4	10.0	12.0	27.1	6.0	7.0
Zn	144.6	155.2	102.5	492.0	49.8	32.2	54.0	32.6	39.8	43.3	48.8	24.4	28.2	34.7
As	0.3	0.8	0.2	0.5	0.2	0.6	0.3	1.3	0.7	0.7	0.3	1.5	0.9	3.4
Cd	606.1	574.6	173.3	1945.8	156.5	195.2	318.9	72.6	150.2	849.3	347.5	115.3	80.7	50.2
Pb	1.8	8.7	0.9	9.1	2.8	4.1	0.3	2.8	0.4	0.4	0.6	10.3	0.6	1.6
Al	357.6	1039.4	175.7	2342.0	769.4	866.8	500.4	1324.0	190.2	534.8	554.0	2304.0	438.2	1066.6
Fe	9214.0	49000.0	1850.0	37760.0	4754.0	9712.0	714.8	10772.0	12198.0	49800.0	608.2	8042.0	2656.0	32040.0
Ca	2074.0	188.4	1040.6	456.0	1537.2	911.0	2072.0	977.8	2184.0	959.8	2850.0	2736.0	4486.0	3010.0
K	23600.0	3316.0	11866.0	8090.0	12874.0	3654.0	10702.0	3626.0	8992.0	4928.0	3686.0	772.6	14270.0	10300.0
Mg	1932.8	379.6	1053.0	735.0	1218.0	413.4	1321.6	686.6	1819.0	543.8	2108.0	443.0	1784.6	1798.4
Na	12510.0	1851.0	1150.6	3450.0	3796.0	676.8	1915.0	4542.0	5420.0	2384.0	19774.0	2176.0	5402.0	6690.0
P	3780.0	1318.0	1073.6	323.8	668.6	510.0	1268.4	404.4	803.0	1202.8	475.6	240.6	1246.2	1099.2
Si	409.6	438.4	335.4	389	267	1104.6	110.3	453.6	503.8	269.2	195.98	653.8	219	348.8

Results presented in Table 4.3 shows that all studied plant species accumulated higher concentrations of Cr, Mn, Cu, Cd, Pb, Al, As, Co, Zn, Ni, Fe and Mg in their roots than in their leaves except for *Cyperus esculentus* and *Phragmites mauritianus* which had higher Cr and Mg content in the leaves as well *Typha capensis* that had higher Cr content in the leaves (Table 4.4). The same trend of high concentration of metals (Fe and Al) in the roots than in the shoots in *Cynodon dactylon, Typha capensis* and *Juncus effussus* was also reported in a study conducted at Upper Olifants catchment by Schachtschneider *et al.,* (2017). The metal content in *Phragmites mauritianus Cyperus esculentus Typha capensis*, and *Cynodon dactylon* followed this trend: Fe > Mg > Al > Cd > Mn > Zn > Cr > Ni > Cu > Co > Pb > As. The *Juncus lomatophyllus* and *Juncus effussus L.* showed a different trend, Mg > Fe > Mn > Al > Cd > Zn > Cr > Ni > Cu > Co > As > Pb. The high concentration of toxic chemical species was observed in wetland plants in sample S4, S7 and S14 whereby *Cyperus esculentus* showed higher concentrations in all the studied chemical species followed by *Juncus lomatophyllus* and *Juncus effussus*. Water showed the least concentration Cr, Mn, Ni and Co while plants accumulated most concentration of these metals, followed by sediments, a similar trend was observed for all sampling points. This indicates that plants and sediments are playing a role in up taking chemical species from the contaminated water. *Cynodon dactylon* has been reported to have higher accumulation capabilities for metals such as Pb, Cd, Zn from mine tailings (Archer and Caldwell, 2004; Gonzalez and Gonzalez-Chavez, 2006; Mulingisi *et al.*, 2009). The bioconcentration potential of *Cyperus esculentus* in a gold mine tailings dam has been reported by Mulingisi *et al.* (2009) and the results showed that the plant species accumulated Mn (223.8 mg/kg), Zn (38.7 mg/kg), Cu (46.7 mg/kg), Pb (6.1 mg/kg), Cd (1.0 mg/kg) and Co (1.75 mg/kg). In this present study *Cyperus esculentus* accumulated Mn, Zn, Cu, Pb, Cd and Co as indicated in Table 4.4.

4.4.4 Translocation and bioconcentration factors

4.4.4.1 Translocation factor

Translocation factor (TF) shows the ability of the plant species to transport or transfer chemical species from the roots to the shoots. If the TF value is greater than 1 then the plant species has the potential to translocate the accumulated. On contrary, if TF less than 1 indicated that high concentration of elements was accumulated in the roots than in the leaves/shoots. Table 4.5 represents the translocation factor (TF) of elements from the roots to the shoots of different plant species.

Table 4.5: Translocation factor of elements in selected plant species.

Cations mg/kg	*C. Esculentus (S1a)*	*P. mauritianus (S1b)*	*C. Esculentus (S4)*	*J. Effussus L. (S7)*	*C. Dactylon (S9)*	*J. lomatophyllus (S10)*	*T. Capensis (S14)*
Cr	0,58	1,27	1,05	0,15	0,61	0,09	1,41
Mn	5,08	0,94	1,26	2,46	1,67	6,37	2,36
Co	0,58	0,12	0,66	0,50	0,47	0,43	0,54
Ni	0,86	0,19	1,56	0,88	0,53	0,99	0,96
Cu	0,89	0,20	0,62	0,78	0,44	0,45	0,86
Zn	0,93	0,21	1,55	1,66	0,92	2,00	0,81
As	0,39	0,28	0,33	0,19	1,05	0,17	0,26
Cd	1,05	0,09	0,80	4,39	0,18	3,01	1,61
Pb	0,20	0,10	0,67	0,12	1,03	0,06	0,37
Al	0,34	0,08	0,89	0,38	0,36	0,24	0,41
Fe	0,19	0,05	0,49	0,07	0,24	0,08	0,08
Ca	11,01	2,28	1,69	2,12	2,28	1,04	1,49
K	7,12	1,47	3,52	2,95	1,82	4,77	1,39
Mg	7,12	1,47	3,52	2,95	1,82	4,77	1,39
Na	6,76	0,33	5,61	0,42	2,27	9,09	0,81
P	2,87	3,32	1,31	3,14	0,67	1,98	1,13
Si	0,93	0,86	0,24	0,24	1,87	0,30	0,63

Figure 4.6 below shows *Cyperus esculentus* at different growth level, collected from (a) discharging point and (b) in a wetland.

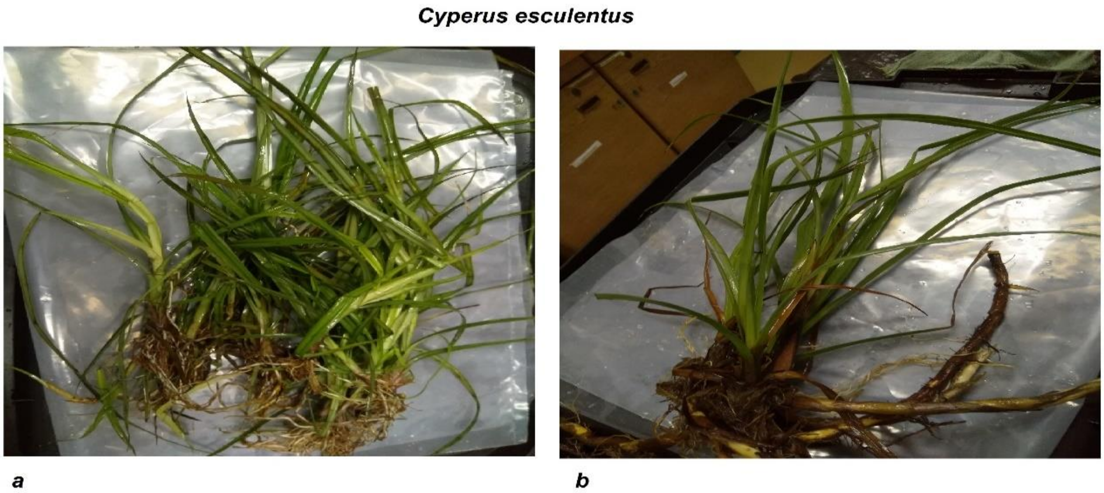

Figure 4.6: *Cyperus esculentus* species from different sampling points, a represent (a) species collected from the discharging point (S1) and (b) was collected from the wetland (S4).

The results in Table 4.4 showed that elements such as Ca, K, Mg, Na and P were translocated (>1) from the roots to the shoot/leaves of *Cyperus esculentus* (S1a) from the discharging point. Similarly, *Phragmites mauritianus* from the same discharging point translocated Cr, Ca, K, Mg and P. Similar species (*Cyperus esculentus* (S4)) collected at the wetland showed translocation factor greater 1 for more chemical species (Cr, Mn, Ni, Zn, Ca, K, Mg, Na, P) compared to the one collected at the discharging point. This could be due to the growth difference as indicated in Figure 4.6, whereby the plant species collected from the wetland showed well developed roots as compared to the one from the discharging point. *Cyperus esculentus* translocated Cr, Mn, Ni, Zn, Ca, K, Mg, Na and P, *Phragmites mauritianus* translocated Cr, Ca, Mg, K, and P, *Juncus effussus L.* translocated Mn, As, Pb, Ca, K, Mg, and P, while *Cynodon dactylon, Juncus lomatophyllus and Typha capensis* translocated Mn, As, Pb, Ca, K, Mg, Na, and Si; Mn, Zn, Cd, Ca, K, Mg, Na, and P and Cr, Mn, Cd, Ca, K, Mg and P, respectively. However, the TF for chemical species such as Co, Cu, Al, and Fe did not exceed one (TF < 1) for any of the studied species. This could be an indication that bulk of these chemical species were accumulated in the roots of the studied plants and little amounts were transferred to the leaves. Amongst the studied plants, *Cyperus esculentus* (S4) translocated more chemical species from the roots to the shoots. The TF values greater than 1 indicate that such particular plant species can accumulate contaminants from the soil to the roots and translocate them to the shoots/ leaves and as such they can be used for the purpose of phytoextraction. On contrary, whereas plants with low TF (<1) can be used for phytostabilization.

4.4.4.2 Bioconcentration factor (BCF)

A BCF of greater than ten implies that a certain plant species is hyperaccumulator of the specific element and has the potential to be used for phytoextraction purposes, while a BCF less than 10 implies the potential to be used in phytostabilization. Table 4.6 presents the bioconcentration factor of chemical species in different plant species.

Table 4.6: Bioconcentration factor of different plant species.

Cations mg/kg	*C. Esculentus (S1a)*	*P. mauritianus (S1b)*	*C. Esculentus (S4)*	*J. Effussus L. (S7)*	*C. Dactylon (S9)*	*J. lomatophyllus (S10)*	*T. Capensis (S14)*
Cr	0,16	0,28	2,52	0,32	0,25	0,76	0,20
Mn	1,87	0,77	8,22	5,81	0,76	25,94	8,95
Co	1,04	0,20	6,68	2,40	0,65	6,66	1,73
Ni	0,94	0,28	8,73	1,83	0,65	5,26	0,98
Cu	0,46	0,19	3,51	0,65	0,70	3,06	0,32
Zn	0,29	0,10	8,01	1,54	0,41	7,75	1,24
As	0,08	0,05	0,42	0,37	0,04	0,28	0,28
Cd	296,37	98,59	12659,43	969,60	970,55	9786,02	568,11
Pb	0,27	0,14	0,53	0,13	0,22	2,11	0,07
Al	0,10	0,14	0,33	0,12	0,06	0,80	0,10
Fe	0,20	0,15	0,89	0,51	0,17	0,35	0,44
Ca	5,10	0,90	10,44	11,70	6,77	10,80	3,57
K	148,79	83,08	36,83	20,92	8,31	30,03	14,49
Mg	12,37	5,43	15,18	7,16	3,87	17,18	2,11
Na	163,68	22,31	41,12	23,19	1,79	269,99	48,25
P	1,39	0,52	22,97	1,17	0,53	8,07	4,85
Si	2,02	1,64	4,00	1,29	2,66	6,64	1,53

From the results in Table 4.6, it is observed that all studied plant samples showed a hyperaccumulation ability of Cd with BCF greater than 10 amongst other metals, hence, they can all be used in phytoextraction of Cd. *Cyperus esculentus* had the highest BCF of Cr (2.52), Co (6.68), Ni (8.73), Cu (3.51), Zn (8.01), and Cd (12659.43). *Juncus effussus L.* and *Juncus lomatophyllus* showed hyperaccumulation potential to Mn (25.94), Ca (11.70); and Mg (17.18), and Na (269.99) respectively, this plant species can be used for phytoextraction. *Cyperus esculentus* showed hyperaccumulation potential of Cd, Ca, K, Mg, and Na and it can be used for phytoextraction of these chemical species. Additionally, BCF of Cr, Mn, Co, Ni, Cu, Zn and Si were found to be below ten, this indicated that *Cyperus esculentus* do not have hyperaccumulation abilities towards these chemical species, however the plant species can be used for phytostabilization of such chemical species. On the other hand, *Juncus lomatophyllus* had BCF greater than one in Co, Ni, Cu, Zn, Pb, P, and Si, and this indicated that the plant do not have hyperaccumulation abilities of these chemical species and as a result it can be used phytostabilization of such chemical species. In addition, *Juncus lomatophyllus* showed hyperaccumulation (BCF>10) of Mn, Cd, Ca, K, Mg, and Na and it can be used for phytoextraction purposes of such chemical species. No plant species show high accumulation (BCF>1) of Fe, Al, and As, this implies that all the studied plant species bioaccumulated those toxic metals in the roots and were not translocated in the above ground plant structure.

4.5. Summary

This chapter presented the physicochemical characteristics of acid mine water collected from mine discharging points, mine water retention ponds, upstream, mid-stream and downstream of the wetland and further investigated retention capabilities of inorganic contaminants by sediments and aquatic plant species. The field parameters ranges are pH (2,53 to 3,60), Eh (194 to 256,8 mV), EC (1066 to 5584 µS/cm), DO (2,94 to 8,24 mg/L), and Salinity (0,82 to 6,09 psu). The metal concentrations in mine water ranged from Cr (2,5 to 36,6 mg/L), Cu (6,8 to 152,8 mg/L), Co (0,41 to 3,65 mg/L), Cd (2,33 to 31,17 mg/L), As (2,28 to 43,17 mg/L), Ni (0,24 to 6,90 mg/L), Mg (31.2 to 190.7 mg/L), Al (14.54 to 89.21 mg/L), Fe (0.55 to 234.9 mg/L), Zn (0.65 to 4.19 mg/L), and Mn (6.10 to 42.27 mg/L). The metal concentrations in the sediments ranged from Cr (26.55 to 92.70 mg/kg), Mn (30.81 to 142.61 mg/kg), Co (1.39 to 114.83 mg/kg), Ni (3.0 to 172.91 mg/kg), Cu (9.74 to 137.86 mg/kg), Zn (9.43 to 6182.69 mg/kg), As (1.80 to 15.12 mg/kg), Cd (0.03 to 21.49 mg/kg), Pb (3.62 to 73.01 mg/kg), Al (3570 to 18442 mg/kg), Fe (16326 to 361600), and Mg (63.38 to 6108 mg/kg). All plant species showed bioaccumulated Al, Mn, Fe, Co, Ni, K, Mg, Na, Si, and Zn thus, they can be used for phytoremediation of land contaminated by AMD. Amongst the studied plant species, *Cyperus esculentus* accumulated almost all of the studied toxic metal species, followed by *Juncus lomatophyllus* and *Juncus effussus.* Therefore, these three plant species showed to be more efficient in retaining more inorganic contaminants and showed potential for use in phytoremediation of AMD. in constructed wetlands. Hence, adsorption and extraction were the main retention mechanisms for inorganic contaminants. Further studies should be conducted to evaluate the impact of seasonal variations with relation to metal uptake by the latter plant species.

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Chapter 5: Conclusion and Recommendation

This chapter gives a summary of the main findings of the study and recommendation for future studies.

5.1 Conclusion

The findings of this study achieved the main objective of bioprospecting naturally occurring plant species surviving in gold mine tailings of Johannesburg crown mines and native plants species in AMD impacted wetlands in eMalahleni, Mpumalanga with potential for use in phytoremediation of mine tailings and AMD. All specific objectives mentioned below were successfully achieved.

The specific objectives set were:

- To characterize the physicochemical properties of gold mine tailings and leachates from collected from Crown Mines, Gauteng Province.
- To identify the plant species surviving in the Gold mine tailings and leachates ponds and further evaluate their inorganic chemical species retention capabilities.
- To characterize the acidic mine water discharging from the decant points into the wetland streams in eMalahleni region of Mpumalanga Province.
- To investigate the inorganic contaminants retention by sediments and further bio-prospect native plant species surviving in the wetlands with better metal retention capabilities.

The study was focusing on characterization of gold mine tailings, leacates, sediments, *Cortaderia selloano* and *Populus alba,* aquatic native plant species, acid mine drainage from Crown Gold Mine and around eMalahleni abandoned collieries, and further evaluate the retention potential of inorganic contaminants by identified plant species. This study came up with the following conclusions based on the findings:

✓ The mine tailings are the source of pollution, they contain potentially toxic chemical species such as Pb, Cd, Cu, Ni, As, Co, Mg and Fe which are leached into the water, and result into water contamination in the neighbouring streams.

- ✓ *Populus alba* and *Cortaderia selloano* are the only two plant species identified on gold mine tailings that are naturally growing and they have the ability to phytostabilize the mine tailings.
- ✓ *Populus alba* and *Cortaderia selloano* have the potential to be used in phytoremediation of mine tailings.
- ✓ The mine water discharging from abandoned collieries is acid mine drainage, containing potentially toxic metals such as Fe, Pd, Cd, Co, Cu, As, Ni and Mg, and contaminating the neighbouring freshwater resources.
- ✓ The water quality was increasing from upstream to downstream of the wetland, and sediments were adsorbing some of the potentially toxic contaminants while plants were accumulating some concentrations of these potentially toxic metals.
- ✓ *Cyperus esculentus*, *Phragmites mauritianus, Juncus effussus, Juncus lomatophyllus, Typha capensis and Cynodon dactylon* are native aquatic plants which were investigated for their uptake of potentially toxic metals, and they all showed potential to be used for phytoremediation in wetlands.
- ✓ *Cyperus esculentus* accumulated almost all of the studied toxic metal species, followed by *Juncus lomatophyllus* and *Juncus effussus,* this shows that they can be used for phytoremediation contaminated water.

5.2 Recommendation

- It is recommended that all plants that were proven to phytoextract pollutants, should be used in pilot scale for the contribution of sustainable mine water and environment in South Africa.
- It is also recommended that all native plant species assessed in this study, should be considered in phytoremediation of AMD in constructed wetlands.
- Future studies must investigate whether *Cortaderia selloana* and *Populus alba* can survive and accumulate inorganic contaminants in AMD.
- There is a need to evaluate the impacts of *Cortaderia selloana* and *Populus alba* in the process of natural remediation of mine tailings.
- Investigation must be conducted to assess the impacts of seasonal variation on bioconcentration of inorganic contaminants by *Cyperus esculentus* and *Juncus lomatophyllus.*

- Further studies must be conducted to determine if *Cyperus esculentus* and *Juncus lomatophyllus* can be used for phytomining of commercial metals.

Appendix A

Table 1A: Major and trace elemental composition of gold mine tailings.

Trace elements mg/kg	Diepkloof G1	Mooifontein1 G2	Mooifontein2 G3
Al_2O_3	54600	53200	76600
CaO	3100	2100	7000
Cr_2O_3	100	200	200
Fe_2O_3	27800	27000	38500
K_2O	7000	5100	10700
MgO	4400	4200	5800
MnO	300	200	400
Na_2O	1000	700	1300
P_2O_5	200	200	300
SiO_2	874300	887300	817800
TiO_2	2700	3300	2900
Sc	9.72	9.56	11.11
V	57.52	56.63	71.56
Cr	207.90	203.20	277.20
Co	16.04	7.89	29.80
Ni	63.65	36.05	97.15
Cu	37.17	56.07	56.65
Zn	70.20	50.05	107.85
Rb	28.00	19.90	44.55
Sr	47.80	40.11	64.48
Y	11.67	9.46	14.81
Zr	176.30	204.05	185.80
Nb	5.73	6.83	6.41
Mo	1.07	1.09	2.92
Cs	1.29	0.96	1.94
Ba	175.85	126.85	270.55
La	27.73	27.14	36.46
Ce	51.31	50.06	67.45
Pr	5.40	5.27	7.26
Nd	19.33	18.92	25.83
Sm	3.32	3.17	4.14
Eu	0.77	0.69	0.99
Gd	2.81	2.36	3.41
Tb	0.38	0.30	0.47
Dy	2.27	1.86	2.96
Ho	0.44	0.36	0.59
Er	1.34	1.08	1.70
Tm	0.19	0.14	0.24
Yb	1.27	0.94	1.57
Lu	0.19	0.16	0.23
Hf	4.69	5.17	4.85
Ta	0.65	0.74	0.71
Pb	14.52	9.27	47.42
Th	5.37	4.80	10.31
U	14.21	4.57	26.29