

**An Integrated Investigation of Static, Kinetic and Water Quality
Testing to Predict Acid Mine Drainage
from A Historical Mining Related Activity into Water Resources.
A Case Study of Wasbank, uThukela Water Management Area,
KwaZulu-Natal,
South Africa**

By

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ABSTRACT

Historical and current coal mining-related activities have negatively impacted both the surface and ground resources and the environment globally, causing water pollution, termed acid mine drainage (AMD). Decades of prior surface and underground coal and gold mining have contributed to acid mine drainage extensively. Elevated concentrations of heavy metals and low pH render water resources unsuitable for consumption across the water-use sectors. Currently, the environmental implication of AMD has severely impacted the water resources from an aquatic, domestic, agricultural and livestock perspective. Whilst this has been observed and documented internationally, minimum research attention is placed on small mining towns in South Africa on the prediction of mine drainage from abandoned coal mining sites and its impacts on water resources. Since South Africa being a water-stressed country, and the province of KwaZulu-Natal facing immense water security, quality and quantity issues, the impacts of mine drainage emanating from abandoned mining sites require complete attention to understand the level of environmental risk and impact caused on the water resources and to ensure comprehensive water resource management decisions for the holistic protection of aquatic ecosystem is made. This study employed the use of AMD prediction techniques to determine the impact of mine drainage effluent from an abandoned mine and its impacts on water resources. Static testing (acid-base accounting-ABA), kinetic leach column testing, geochemical, mineralogical analysis of the coal discard (waste rock) and water quality analysis formed part of the integrated investigative research. The study findings indicated ABA and net acid generation (NAG) tests classified the samples as potentially acid-forming (PAF). The samples of all five sampling points (S1-S5) on the abandoned coal discard dump were acid-producing with the following observed, the discarded material had significant sulphur content, positive net acid-producing potential (+NAPP) equivalent to an acid neutralising capacity (ANC)/ maximum potential acidity (MPA) less than 1, (ANC/MPA ratio <1), the final net acid generation pH (NAGpH) is less than 4.5, (NAGpH <4.5) and the ANC/MPA ratio <1 . Samples S1 to S5, yielded high organic matter and the total carbon percentage ranged from 40.21% to 60.84%. The combination of the NAG and NAPP tests proved to be a better reflection of the site acid mine potential. The kinetic test (leach column testing) was then followed to determine the leachate chemistry of the discard. The test duration was conducted for five samples (five columns) over a 22-week test duration of leachate collection and analyses were made for pH, EC, Na, K, Al, Ca, Cu, Fe, Hg, Ni, Pb, SO_4^{2-} and Cl as well as geochemical analysis. The leachate results were compared to the Department of Water and Sanitation (DWS) Target Water

Quality Range (TWQR). The mean pH is indicative of the general acid nature of the leachates. Na, K, Cu, Ni, Zn and Cl are largely within the acceptable mean concentration range, however the other analytes show great variability, often in concentrations that are toxic. The discard was further analysed by conducting ICP trace metal analysis, and X-Ray fluorescence (XRF) for major and trace metal analysis. The findings indicated very high amounts of Ba (453.17ppm), Sr (360.80ppm) and Zr (127.08ppm); moderately high amounts of V and Ce (30 – 99 ppm); moderate amounts (20 – 30 ppm) of Cr, Cu, Y and La; and, low Sc, Co, Ni, Rb, Zn, Y, Nb, Mo, La, Pr, Nd, Sm, Eu, Ho, Gd, Tb, Dy, Er, Yb, Lu, Hf, Ta, Th, Pb and U. Evidently some trace elements in coal are radioactive, these included uranium (U) and thorium (Th) of the composite sample. Mineralogical analysis using X-Ray diffraction technique (XRD), identified the following mineral phases: quartz, kaolinite/dickite, illite/muscovite and gypsum with a crystallinity index of 58%. Water quality sampling of the two water resources (Biggargatspruit and Wasbank River) was conducted for a test duration of 28 months. The water quality compliance levels for fitness of use indicated compliance and non-compliance levels to the DWS TWQR, Six parameters, Fe (58%), K (55%), pH (54%), Ca (52%), SO_4^{2-} (46%), Ni (46%) complied with the DWS TWQR, and 11 parameters were in exceedance of the DWS TWQR that ranged within the chronic and acute effect value range. These include Al (61%), TDS (59%) Cr^{6+} (55%), Cu (55%), Na (54%), Hg (45%) EC (45%), Zn (36%), Pb (27%), Cl (27%) and Cd (16%). The WQI further indicated the water quality at these sites is unacceptably unfit for domestic use (S2, S3 and S4) to very poor water (S1 and S5). In addition, to determine the inferences in the study from the results, multivariate analysis, the Kruskal-Wallis Test and a post-hoc Mann-Whitney U test were performed. The tests indicated a statistically significant difference across the sampling sites. The findings indicated the successful prediction of AMD from the abandoned coal discard dump, the impacts of the coal discard leachate quality on the water resources, mine waste characterisation, environmental pollution and recommendations for mine water management and resource protection.

As the candidate's supervisor, I have approved this thesis for submission.

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Name: Dr Ajay Bissessur (Co-Supervisor)

Date: 27 March 2025

PREFACE

The experimental work described in this dissertation was carried out in the School of Agricultural, Earth and Environmental Sciences, University of KwaZulu-Natal, Durban, Westville, from October 2017 to December 2023, under the supervision of Dr Srinivasan Pillay.

These studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others it is duly acknowledged in the text.

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I, Srinivasen Govender (Pr.Sci.Nat), declare that

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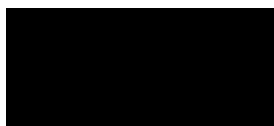
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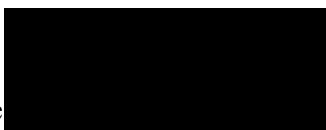
DETAILS OF CONTRIBUTION TO PUBLICATIONS that form part and/or include research presented in this thesis (include publications in preparation, submitted, *in press* and published and give details of the contributions of each author to the experimental work and writing of each publication)

Publication 1: An Assessment of the impacts of the Indumeni coal discard dump on the Water of Biggarsgatspruit and Wasbank Rivers, KwaZulu-Natal, South Africa.

Publication 2: The Characterization of Acid Mine Drainage using static testing at the abandoned Indumeni Discard Dump Site (IDDS), uThukela Water Management Area, KwaZulu-Natal, South Africa.

Publication 3: Kinetic Testing of Acid Mine Drainage from the Indumeni Discard Dump Site, Klip River Coalfields, KwaZulu-Natal, South Africa.

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LIST OF ABBREVIATIONS

ABA	Acid Base Account
ABCC	Acid Buffering Characteristic Curve
AER	Acute Effect Range
AEV	Acute Effect Value
AG	Agricultural
AGSA	Auditor General South Africa
ALD	Anoxic Limestone Drains
AMD	Acid Mine Drainage / Acid and Metalliferous Drainage
AMIRA	Australian Minerals Industry Research Association Limited
AMSL	Above Mean Sea Level
ANC	Acid Neutralising Capacity
AR	Assessment Reporting
ARC	Agricultural Research Council
ARD	Acid Rock Drainage
ASTM	America Society for Testing Materials
ATE	Average Treatment Effect
CAF	Central Analytical Facility
CEV	Chronic Effect Value
CHNS	Carbon, Hydrogen, Nitrogen, Sulphur Elemental Analyser
CSIR	Council for Scientific and Industrial Research
D	Domestic
DEA	Department of Environmental Affairs
DO	Dissolved Oxygen
DWA	Department of Water Affairs
DWAF	Department of Water Affairs & Forestry
DWS	Department of Water and Sanitation
EC	Electrical Conductivity
Eq.	Equation
GARD	Global Acid Rock Drainage Guide
GPS	Global Positioning System
HCL	Hydrochloric Acid
ICDD	International Centre for Diffraction Data
ICP-OES	Inductively-Coupled Plasma Optical Emission Spectrometry
ISC	Ion-Selective Electrode
IDDS	Indumeni Discard Dump Site
INAP	International Network for Acid Prevention
MANOVA	Multivariate Analysis of Variance
MHCL	Molarity of Hydrochloric Acid
MASL	Meters Above Sea Level
MPA	Maximum Potential Acidity
MWM	Mine Water Management

MWQ	Mine Water Quality
MPRD	Mineral and Petroleum Resources Development
MTSF	Medium Term Strategic Framework
NECSA	South African Nuclear Energy Corporation
NEMA	National Environmental Management Act
NAPP	Net Acid Producing Potential
NAG	Net Acid Generation
NWA	National Water Act
NWRS	National Water Resource Strategy
pH	Potential of Hydrogen
PAF	Potentially Acid Forming
RF	Radiofrequency
RSA	Republic of South Africa
SA	South Africa
SANBI	South African National Biodiversity Institute
SANS	South African National Standards
SAWS	South Africa Weather Services
SAWSA	South Africa Weather Services Annual Report
SDG	Sustainable Development Goal
SI	Sub Index
STATSSA	Statistics South Africa
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TWQR	Target Water Quality Range
UDM	uMzinyathi District
UMDM	uMzinyathi District Municipality
UN	United Nations
WHO	World Health Organization
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
WMA	Water Management Area
WQI	Water Quality Index
WRC	Water Research Commission

LIST OF UNITS

°C	Degrees Celsius
cm	Centimetre
g	Grams
J/cm²	Joules per square centimetre
kg	Kilogram
km	Kilometre
L	Litre
L/min	Litre per minute
m	Metre
M	Molarity / Molar concentration
mg/L	Milligrams per litre
ml	Millilitre
mm	Millimetre
mS/m	Milliesiemens per metre
n.d.	No date
NTU	Nephelometric turbidity units
t	Tons
µm	Micrometre / Micron

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THESIS DEDICATION

***I DEDICATE MY PHD THESIS TO MY PRECIOUS
DAUGHTER, YUVANYA GOVENDER
AND
WIFE, MRS ASHENDREE GOVENDER***

CHAPTER ONE

1.1 Introduction

Worldwide, abandoned coal mines and discarded dumps have created enormous volumes of waste that have resulted in widespread water pollution (Paktunc, 1999; Kagambega *et al.*, 2014; Acharya and Kharel, 2020). This is a direct result of poor mine closure and water management practises in the global mining industry resulting in geochemical processes that promote acid mine drainage (AMD)/acid rock drainage (ARD), subsequently resulting in pollution of the freshwater resources and the environment.

According to Ighalo *et al.* (2022), pp.37, AMD is termed: “*A multi-factor pollution formed from complex chemical, physical, and biological interactions that take place under ambient conditions in abandoned and active mines*”. AMD is produced by the oxidation of sulphide minerals, iron pyrite or iron disulphide (FeS_2) (McCarthy, 2011; Fadiran *et al.*, 2013; Park *et al.*, 2019) and facilitated biochemically by bacteria, specifically *Thiobacillus ferrooxidans* and *Ferroplasma acidarmanus* (Fadiran *et al.*, 2013). This natural chemical reaction can further advance when minerals are exposed to the ingress of air and water (Jennings *et al.*, 2008; Dutta *et al.*, 2018; Park *et al.*, 2019). The resultant acidification and sulphur oxidation lead to both chemical and microbial discharge of pollutants containing elevated levels of toxic substances and heavy metals (Chotpantararat, 2011). In turn, this contributes negatively to the water quality (Pope *et al.*, 2006) due to elevated concentrations of heavy metals, sulphates, total dissolved solids, and increased acidity (Smith, 1997). In addition, the minerals formed during the AMD process can further precipitate into the stream bed of the water resources and impact benthic organisms (Hodsgen and Harding, 2012; Masindi *et al.*, 2022). The resultant poor-quality water is unsuitable for use across water use sectors, and the extent of environmental contamination globally necessitates quantification. Verburg *et al.*, in 2009 noted that AMD/ARD research has been going on for more than 50 years with accelerated progress noted in the two decades prior to their publication. Belmer *et al.*, 2014 contended that there was limited investigation on the magnitude and impact of coal mine wastewater discharges into uncontaminated and unmodified catchments. Wang *et al.*, 2021 further documented that extensive research has been conducted with respect to the formation, impact, migration, prediction, and treatment of acid mine drainage. Currently, this is a global, national, and provincial environmental problem leading to major degradation of freshwater resources and the surrounding environment.

1.2 Contextualization of the Problem

Acid mine drainage (AMD) is the cause of high metal concentrations in contaminated effluents (Ferguson and Erickson, 1987) and exceptionally low pH, hence generating sulfuric acid [H_2SO_4], dissolved iron [$\text{Fe}(\text{OH})_2^+(\text{aq})$], and ferric hydroxide precipitate [$\text{Fe}(\text{OH})_3$]. AMD is caused by surface and underground mining activities occurring over several decades due to a rapid increase in coal production (Matsumoto *et al.*, 2016). Metal contamination in seepage and run-off originates from tailings and waste rock composed of sulphide minerals (pyrite [FeS_2] and pyrrhotite [$\text{Fe}_{(1-x)}\text{S}$]) and, with specific reference to the mining of coal resources, this problem is globally widespread (Lawrence *et al.*, 1989) that has intensified over time.

South Africa's history of coal mining spans over 100 years (Mathu, 2014) and coal production is an important foreign exchange earner for the country. During this period, several of the now abandoned coal mines remain un-rehabilitated. There were 5 906 abandoned mines that needed to be rehabilitated as at end May 2008 (Auditor General, 2009), however, the audit finding in the AGSA (2021) report indicated that there are 6100 derelict/abandoned mines that the Department of Mineral Resources and Energy (DMRE) is managing (AGSA, 2022). Detrimental environmental impacts from several of these mines continue to create a major strain on the scarce water resources of the region whilst simultaneously endangering vulnerable ecosystems (Auditor General, 2009). Currently, the exact figures of abandoned, derelict/ownerless mines are unknown but may well be close to those mentioned by the Auditor General's report. This is indicative of a knowledge gap in attempts to quantify AMD environmental impacts upon the water resources of this country. Currently the critical environmental challenge facing South Africa is acid mine drainage from past (abandoned mines) and present mining operations, (Baloyi *et al.*, 2023). Subsequently creating serious environmental pollution that is extreme in toxicity, heavy metals and acidity (Mwewa *et al.*, 2002). The problems associated with such impacts, are water levels rising in mine voids above the critical environmental limit and decanting into the environment and surface and ground water resources (Lourenco and Curtis, 2021). Toxicity impacts experienced are biotic impacts on aquatic organisms, alteration of habitats, changes on stream sediment (orange/yellow staining) and the disruption of the nutrient cycles and other mechanisms (Skousen *et al.*, 2019). This consequence is site-specific for aquatic ecosystems, water resources and the respective catchments within South Africa, However, every mine (site-specific) is unique in terms of its AMD potential (Akcil and Koldas, 2005). The waste from mine dumps, principally mine tailings, is considered among the largest mining waste on the earth (Dold, 2014). Subsequently,

mine wastes impacts can be diverse, and such impacts include water, soil, air pollution, and toxicity, biodiversity loss, geo-environmental disasters, and economic wealth forfeiture (Wong, 2003; Sheoran *et al.*, 2008 cited in Sheoran *et al.*, 2010) and may thus present deleterious consequences. To ascertain the environmental and economic liability of acid mine drainage in this country remains challenging to date (Baloyi *et al.*, 2023), however the removal of contaminants and metal from the impacted mine water has inevitably become an urgent necessity (Mwewa *et al.*, 2002) as this country is experiencing water-scarcity (Crookes *et al.*, 2018; Mutamba, 2019) and the existence of major risks with water availability and resource requirements (Mutamba, 2019) are further evident, hence the necessity to protect the water resources from AMD.

To prevent AMD from leaching into the water resources and the environment, effective prediction techniques are used as a tool for long-term mine water and water resource water quality management. The extensively used method to determine the AMD potential rates is Acid Base Accounting (ABA) (Skousen *et al.*, 1987 and Skousen *et al.*, 2019). This procedure evaluates overburden/discard chemistry (Skousen, 2017). The outcome of this assessment is then followed by the kinetic leach test for mine water quality (MWQ). Mine water quality prediction is based as follows: waste material test leachability occurring in field and laboratory condition; hydrological, mineralogical, and chemical characterisation, geological and geochemical assessment of waste material; and modelling (G.A.R.D, 2013).

Currently, there exists a knowledge gap on the impact of acid mine drainage from abandoned coal discard dumps in KwaZulu-Natal. The contribution of this research will augment policy formulation and strategy implementation to be exercised strategically and efficiently by the state to improve mine water management by reducing the impacts of acid mine drainage from post-mining activities. Henceforth it is within this context that this study focuses on the prediction of acid mine drainage to ascertain the potential rates and impacts of AMD using static testing, kinetic testing, (laboratory-based) and water quality analysis (field-based) on a historical mining site in the uThukela Water Management Area of northern KwaZulu-Natal.

1.3 Study Site

The targeted study area is an abandoned coal discard dump mining site (Indumeni Mine Dump) (Figure 3.2) that is located within the Klip River Coal Fields in the Wasbank area within the Sandspruit Catchment (uMzinyathi District). Coal discard sampling of the actual mine dump

and surface water quality sampling of water resources in the vicinity of the study area were conducted to predict acid mine drainage. A detailed description of the mine's characteristics and history is given in Chapters 2 and 3, respectively.

1.4 Aim of the Study

The aim of this study is to assess acid mine drainage (AMD) rates and potential impacts from discarded coal (mine waste material) of a non-operational mine in the uThukela Water Management Area using static and kinetic testing methods as well as water quality analysis of the water resources in the surrounding area: A case study of the Indumeni mine and Sandspruit catchment, Wasbank, KwaZulu-Natal.

1.5 Objectives of the Study

- ❖ To conduct a survey of the Sandspruit Catchment including, *inter alia*, physiographic characteristics, mining history and possible future environmental impacts.
- ❖ To assess the water quality of the Sandspruit Catchment at pre-selected sampling site. The sampling framework is designed to reveal the extent, if any, of contamination from the target disused mine.
- ❖ To extract coal samples from the discard coal dump of the Indumeni discard coal dump. These samples would then be:
 - Analysed for their geochemical properties; and
 - Used to conduct the static and kinetic leach tests.
- ❖ To use the results from the acid tests and the water quality assessments to
 - make inferences of the acid-generating potential of the accumulated discard coal; and
 - To relate changes of water resource quality to mining activities.
- ❖ Finally, to suggest improvements where appropriate for mine water management.

1.6 Relevance of the Study

According to the United Nations, by the year 2050 expectations for the demand of water is to increase by 55%. This growing concern of declining water quality is impacting human well-being, environmental sustainability, and economic performance (UN-Water, 2015). It is within this context that the study is extremely relevant and significant for mine water management, mine waste characterisation, and freshwater protection. This relevance is directly linked to the outcomes of the Sustainable Development Goals (SDGs) and it is envisaged that the outcome of this research will contribute to the achievement of following SDGs: SDG 3 (Good health

and well-being); SGD 6 (Clean water and sanitation); SGD 13 (Climate action); SGD 14 (Life below water); SGD 15: (Life on earth) and SGD 17 (Partnerships for the goals).

Currently South Africa has made significant progress in achievement of the SDGs with the main contributions as follows: economic (11.2%), environment (10.1%) and social (9.5%) (STATSSA, 2023). The outcomes of the above have been achieved through the alignment of the country's short-and long-term planning tools, i.e. the National Development Plan (NDP), Medium Term Strategic Framework (MTSF), departmental strategic and annual performance plans (STATSSA, 2023). This study is further linked to the outcomes of the National Water Resource Strategy of South Africa (NWRS), a comprehensive framework that ensures protection, sustainable equitable access and water security for all sectors utilising the countries water resources (DWS, 2003b).

In addition, to ensure the safe quality of water for aquatic, domestic, agricultural and industrial uses, stringent control measures will need to be implemented for comprehensive water resource protection as outlined in the National Water Act (NWA) (Act 36 of 1998), Chapter 3: Protection of water resources and Chapter 4: Use of Water; the National Environmental Management Act (NEMA) (Act 107 of 1998), Chapter 5: Integrated Environmental Management and Chapter 7: Compliance, Enforcement and Protection, the Mineral and Petroleum Resources Development Act, of 2002, together with the latest Mine Water Management (MWM) policy of 2022, These address the problems associated acid mine drainage and mine water from abandoned, ownerless, current and future mines and further sets out the norms, standard and values for mine water management in South Africa (DWS, 2022).

Subsequently the AMD predictive investigation, assessment and recommendations emanating from this study will provide a benchmark that may be used within South Africa and internationally to enhance mine water management from abandoned coal mine dumps. This will assist in the prevention or mitigation (frequency of recurrence of AMD) of mine water pollution, enhance mine waste characterisation, and develop rehabilitation measures for short, medium, and long term for mine water resource management and protection. This together with the compliance and monitoring of issued authorizations (mining and water use licenses) will minimise waste and pollution control (from AMD/ARD) into the environment. Furthermore, the adherence to authorisation conditions listed in the mining and water use licenses issued to the mines and the effective implementation of compliance monitoring and enforcement regulation of the license conditions by the government will aid in reducing the pollutant impact

thus protecting the environment and scarce freshwater resources. This pro-active and strategic approach between the government and the private mining sector will strengthen collaboration in this water-stressed country, South Africa.

1.7 Chapter Formation and Sequence

Chapter two of this dissertation focuses on the literature review for AMD from a global, national, and provincial perspective, acid mine chemistry and geochemistry, prediction techniques/methods, mine water management, the impacts of acid drainage on water resources and surrounding environment, government policies and guidelines. Chapter three, the study area and Chapter four details the methodology adopted for the research. Chapter five encompasses the results from water quality analysis (river water samples), static and kinetic testing (leachate from kinetic testing), and geochemical analysis. The results are presented in the form of three scientific papers, respectively. The sixth and final chapter comprises the discussion, recommendations and conclusions of the study.

1.8 Conclusion

Poor mine water management practices have caused wastewater pollution from abandoned mines resulting in AMD subsequently impacting on freshwater resources and the environment, with all life forms in these resources being affected. As a result, the uptake of water for human and livestock consumption, as well as agricultural activities, has become challenging and unsuitable for use.

Information above provides an overview of AMD and the approach to this study however the impact of this type of pollution affecting the water resources, predictive techniques (acid-base accounting-ABA and kinetic leach tests) and water quality analysis will be clearly discussed in the thesis to determine the impact of acid generation and implications thereof.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter encompasses a detailed literature review of the study. The detailed literature review focuses on significant areas that are relevant to the prediction and generation of acid mine drainage from coal discard dumps, the impact of the mine discard waste and effluent drainage into the freshwater resources, geochemical and water quality analysis, review of legal requirements (strategies/policies) for mine water effluent quality and mine water management and the impacts thereof.

2.2 Water, A Global Threat

Freshwater is a crucial resource on land, supporting human societies, terrestrial life and ecosystems and biodiversity. This water is stored in various reservoirs, which are unevenly distributed across different climatic and geophysical environments (Papa *et al.*, 2023). The cryosphere contains about 68,5% of all fresh water on earth that is stored in glaciers and ice sheets, with the remaining 31% in aquifers, wetlands, rivers, lakes, floodplains, and soil moisture (Stephens *et al.*, 2020). Surface waters are significant as they support diverse environments globally and provide important benefits and services to sustain ecological habitat stability, economic activities and human health (Cheng *et al.*, 2022; Papa *et al.*, 2023). Currently, this finite resource is inevitably facing threats from anthropogenic impacts and climate change impacting the quantity and quality of water availability for use.

Globally, water resources management in various countries worldwide poses significant challenges. These include the complexities and vulnerabilities essential in managing such resources, i.e. the rapid pace of industrialization and urbanization, the impact of environmental changes (climate change and global warming) and geopolitical instability. The increase in water stress and shortages in many countries across the globe is one of the most significant obstacles to achieving sustainable progress. (Yuan and Lo, 2022; Salem, *et al.*, 2022).

The climate change intergovernmental panel identified 10 key findings during its six-assessment reporting (AR6) that must be known to all. The report details the global impact

of climate change. Finding number 2 is titled: “Climate impacts on people and ecosystems are more widespread and severe than expected, and future risks will escalate rapidly with every fraction of a degree of warming.” This will eventually have deleterious impacts on the water resources, ecosystems, and human population. According to Apraku *et al.*, (2021), changes in global climatic conditions increased concentrations of atmospheric warming and greenhouse gases. This leads to glaciers melting, increasing sea levels, and precipitation pattern changes which have resulted in negatively impacting human health, ecosystems agriculture, biodiversity, and socio-economic indexes.

The impact of global warming has led to severe water scarcity being experienced by approximately half of the global population (Boehm and Schumer, 2023). Papa *et al.*, (2023) indicate that climate change and anthropogenic stressors have significantly threatened the water resources and freshwater availability to ensure the demands of sustaining population growth, agriculture, and industries. The increased temperatures and drought conditions have exacerbated the spread of vector-borne diseases and declined the productivity of agriculture in Africa presently (Boehm and Schumer, 2023). Currently, the demand for all water-related goods and services has increased significantly, placing the ecosystems and humans at risk. While demand increases, the supply of clean water is diminishing due to the rising pollution of inland waterways and aquifers. (Mishra, 2023).

In the southern African Continent, projections of climatic variations include the intensity of extreme weather conditions (high temperatures and drying conditions) (Nhemachena, *et al.*, 2020). The increase in these temperatures will be higher than the global average, with the semi-arid and western parts being most impacted. Countries including Namibia, Botswana and South Africa would be most affected by the warming conditions. (Nhemachena *et al.*, 2020). According to CSIR (2019), climate change projections for South Africa indicate a rapid annual average temperature rise for the period 2021 to 2050, with the annual average temperatures in the interior expected to rise by 1.5 to 2 times higher than the global rate of increase average. Increased temperatures of more than 4 degrees Celsius are expected and may rise to 7 degrees Celsius in the interior, subsequently, the increased temperatures projected will have significant impacts across the water use and energy sectors (CSIR, 2019).

Subsequently, the projected climate and environmental change will cause extreme variations in rainfall, a pronounced impact on the periods of flood and drought, and water scarcity. Consequently, affecting the livelihood of the human population, agriculture, and mining

activities in the semi and arid regions (Anawar, 2013). Concerning climate change in the mining sector, both surface and groundwater resources will be threatened due to pollution emanating from the mining waste. This waste resulting from the mining activity that contains sulphates, iron and heavy metals is termed acid mine drainage (AMD) (Thomas *et al.*, 2022).

2.3 Brief History of Coal Mining

South Africa is ranked as one of the most resource-abundant countries globally producing gold, platinum and coal thus contributing immensely to social and economic development for centuries (Matsumoto *et al.*, 2016). According to Wang (2023), 21% of the mining sector employees were employed in the coal mining sector and in 2021, 9300 employees were employed in the coal mining sector in this country. In addition, significant growth in both the economy and resource development has been evident (Matsumoto *et al.*, 2016). Coal firms such as Xstrata Coal, BHP Billiton's Energy Coal South Africa (BECSA), Anglo American Thermal Coal, Exxaro Resources, Xstrata and Saso Mining are producing an estimate of 80% of the coal in South Africa with coal reserves estimations of 15 to 55 billion tons (Wang, 2023). The type of coal reserves available are classified; accordingly, anthracite (2%), metallurgical (2%) and bituminous (96%) (Wang, 2023). In the Mpumalanga Province 60% of land is being subjected to prospecting and mining rights (Simpson *et al.*, 2019). Whilst the increase in prospecting and mining rights escalated, it is estimated that 72% of the remaining coal reserves are in the Soutpansberg and Waterberg area (Webb, 2015; Simpson *et al.*, 2019). As such coal mining is contributing significantly to the energy sector providing 70% of South Africa's primary energy source. The country received 90% of its electricity from coal generated power stations (Jeffrey *et al.*, 2014). Whilst natural energy sources are forecast for the country, coal will remain the primary energy source due to its low cost, resource abundance and the exporting of bituminous coal to countries such as China, Europe, and India (Jeffrey *et al.*, 2014).

2.4 Discovery of Coal

The discovery of coal was documented during 1838 and 1859. Currently, coal is found in the 19 coal fields of South Africa. The greater amounts of coal are located in Free State, Limpopo, Mpumalanga, and KwaZulu-Natal while Gauteng, Eastern Cape and Northwest provinces contain lesser quantities of coal (Jeffrey *et al.*, 2014). The coal is mined from both opencast and underground mines. Opencast mining contributes 53%, underground mining using board and pillar methods contributes 40%, stoping contributes 4% and longwall mining contributes 3% of the mined coal (Jeffrey *et al.*, 2014).

Whilst South African mining history has contributed immense economic benefits, this activity has created major environmental problems due to poor mine water and environmental management once mining is completed (Coetzee *et al.*, 2010). One of the problems created is the management of coal waste/discards which has devastating impacts on human health and the environment (Welch *et al.*, 2021).

2.5 Coal waste dumps

The most common form of mine waste is from waste rock. This waste stream is stored in dumps in varying amounts and sizes containing heterogeneous mixtures of inter-burden, overburden, and low-grade coal. (Muniruzzaman and Pedretti, 2021; Welch *et al.*, 2021). Coal waste rock is different from conventional waste rock because it may contain a significant amount of organic carbon. This carbon can directly and indirectly influence the movement of metals and other redox-sensitive elements, for example through oxidation (Vriens *et al.*, 2019). Additionally, the presence of organic carbon can lead to spontaneous combustion, which alters the physical and chemical properties of the waste rock dumps, affecting the mobility of contaminants of interest (COIs) (Welch *et al.*, 2021). The quantity and quality of mine waste/coal waste varies depending on the climatic conditions, site location, mining techniques adopted and waste rock properties. The biological, geochemical, hydrological, and physical processes taking place with the dump determine the waste rock drainage quality (Vriens *et al.*, 2019). The neglect and nonattendance of coal waste dumps are major contributors to leachate runoff, surface and groundwater acid mine drainage contamination, atmospheric pollution, spontaneous combustion, landslide, erosion, and sedimentation (van Breugel *et al.*, 2019). Subsequently, the leachate enriched with metals and metalloids is causing deleterious acid mine drainage impacts on the environment and degrading the water quality (Muniruzzaman and Pedretti, 2021).

In KwaZulu-Natal abandoned mines have caused significant water quality issues, however, 20 mining dumps within this catchment have been rehabilitated by the former Department of Water Affairs and Forestry (DWAF) (DWS, 2014). This was according to an agreement between the former Department of Water Affairs and Forestry (DWAF) and the Chamber of Mines. (DWS, 2014). DWAF ensured responsibility of abandoned mines pollution control and prevention prior to 1956. In addition, where mines were granted closure certificates, the pollution control maintenance would be undertaken by the Department. (DWS 2014).

2.6 Environmental pollution

Significant environmental problem facing the global industry of mining is acid mine drainage. The acid generation process is associated with the oxidation of pyrite and contaminated drainage from the abandoned mines has severely polluted water resources (Weber *et al.*, 2006). In many countries, the AMD has caused irreversible environmental impacts and the continuous discharge of polluted water into the system has caused biological migration (Wang *et al.*, 2020). The impacts of acid mine drainage (mines that contain 1% to 5% of sulphur) on water resources lower the pH, and increase levels of suspended solids, heavy metals, and dissolved solids. Impacts from non-acid-producing mines are neutral mine drainage and impact the hardness of water, total suspended solids, and bacterial contaminants (Kamble, Kumbhar., 2019). Burning coal dumps further impacts the environment, by gaseous emissions comprising mineral phases of iron, fluorine, arsenic, lead, fluorine, and tin are condensed with other elements (Agboola *et al.*, 2020). This creates efflorescent minerals on the waste surface. Organic condensates that are water-soluble are further found on waste surface. (Agboola *et al.*, 2020).

2.7 Acid Mine Drainage (AMD)

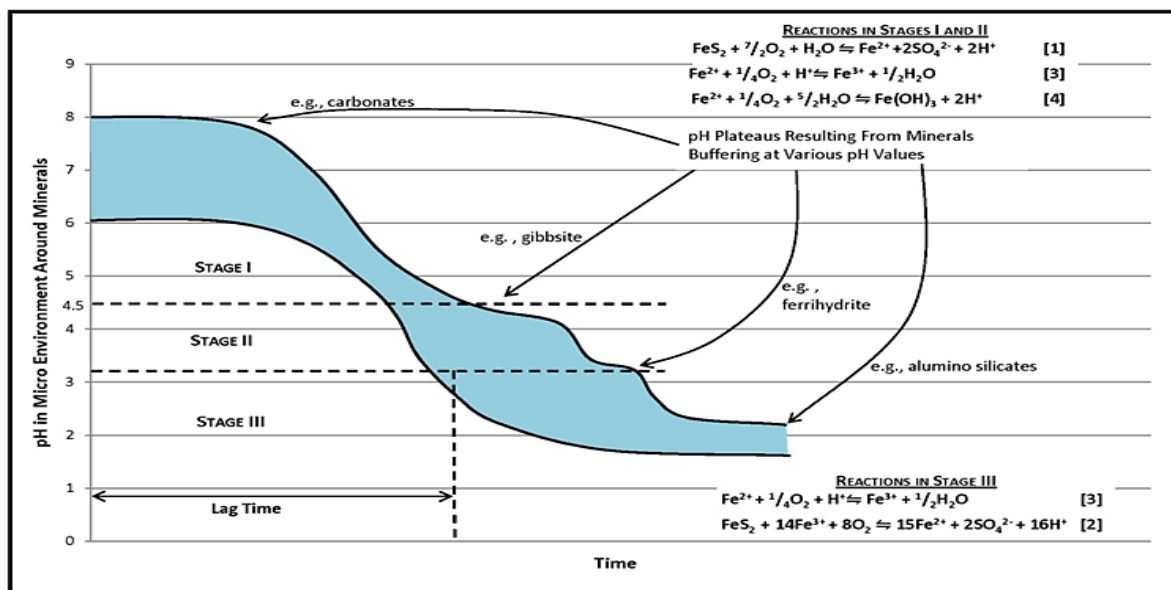
In many countries around the world, one of the main pollutants derived from historic and current mining activities is acidic mine drainage or rock drainage (AMD)/(ARD) (Sinate and Ndlovu, 2014). Consequently, AMD emanates from underground mines and pits, tailings and mine waste rock (Akcil and Koldas, 2006). This environmental hazard has not subsided after decades of research and continues to impact the environment (Rambabu *et al.*, 2020), causing worldwide river pollution (Wang, *et al.*, 2020). AMD generation results from the oxidation of sulphide minerals, iron pyrite and other heavy metals when in direct exposure to oxygen and water (Druschel *et al.*, 2004). Though this process is naturally occurring, mining can promote AMD by the increased quantities of the exposed sulphides and the naturally occurring bacteria can increase the production of AMD by breaking down the sulphide minerals (Skousen *et al.*, 2019). This exposure and the oxidative enhancement of the sulphide mineral pyrite (FeS_2) generate acidic and metal-rich waters (Druschel *et al.*, 2004) upon infiltration into mines and waste rock environments (Sharma *et al.*, 2020) and are further dependant on the mineralogy of the local environment (Akcil and Koldas, 2006).

The significance of this hydro-geochemical weathering is focused on the impact of the drainage leachate from abandoned coal discard dumps (mine waste dumps) into the catchments. Wang *et al.*, (2022) indicate that AMD problems from abandoned coal mines presently are a global concern, subsequently, enormous volumes of tailings are often produced from mining activities

which encompass significant quantities of sulphide minerals (Hassan *et al.*, 2015). In precise reference to coal mines, pyrite and marcasite (FeS_2) minerals are fundamentally responsible for AMD, hence pyrite oxidation reaction requires the supply of adequate amounts of oxygen and water (Pinetown *et al.*, 2007), and microbial processes (Sharma *et al.*, 2020). Henceforth AMD is characterised by high/strong acidity, sulphate, heavy metals, and other toxic elements such as Al, Mn, Fe, Ni, Na, Mg, Cu, Ca, and Pb are causing severe contamination of soil, ground and surface water (Al-Zoubi *et al.*, 2010) Evidently this seepage water and run-off containing sulphide minerals has become a common problem at various mining sites globally (Lawrence *et al.*, 1989).

This environmental problem is a complex chemical process that is determined by a range of biological, chemical and physical factors (Sinate and Ndlovu, 2014) as a result the acid production and consumption rates of balance determines the mine waste effluent drainage quality (Devasahayam, 2006). Drainage effluent quality can be characterised into acidic (pH 0–5); circumneutral (pH 6–8) and or strongly basic (alkaline) (pH 8–12) with possibilities of being radioactive, corrosive, and highly toxic (Nordstrom, 2011). This combination of acid and neutral mine drainage and reactions in stages is reflected in Figure 2.1 below.

Ojonimi *et al.* (2019), state that the quantification of the pollution contamination into water resources and the land by AMD is yet to be determined and its uncontrolled release into the environment poses a serious impact. This is evident globally, nationally, and provincially leading to major harmful degradation and destruction of the environment and water resources.



2.8 Acid Mine Drainage Sources

AMD sources are dependent on the type of mining and mineral processing methodology adopted (INAP, 2014), subsequently, the sources of AMD are potentially from active, inactive, abandoned mine sites, open pit mining sites and mine waste sites (Alegbe *et al.*, 2019). The primary sources of acid mine drainage include the following: coal discarded dumps, open pit and underground mines workings, tailing dams, dewatering pumped and naturally discharged underground water, pollution by diffuse source from rehabilitated areas, and construction rocks (Akciil and Koldas, 2006; Kaur *et al.*, 2018). The secondary sources include treatment sludge ponds, rock cuts, stoke piles, concentrated spills along the road and emergency ponds (Akciil and Koldas, 2006; Kaur *et al.*, 2018). The oxidation of sulphide minerals is the main source of AMD, particularly iron pyrite (FeS_2) (known as fool's gold) (Kefeni, *et al.*, 2017). AMD is determined by the following components: reactive sulphides, sulphide minerals, elemental sulphur, different sulphur intermediates, molecular oxygen, and water in the mine waste material (Kaur *et al.*, 2018). Additionally, the pH, temperature, bacterial activities, presence of different oxidants (e.g. Fe^{3+} , Mn^{3+} or Mn^{4+}), and alkaline and buffering minerals are alternate factors affecting the rate of acid generation (Kaur *et al.*, 2018). A significant number of microorganisms inhabit the AMD environment irrespective of the acidity, heat, sulphate, and heavy metal concentrations. The microorganisms contribute to the formation of the chemoautotrophic biosphere at the surface. The microorganism utilizes the electron donors acquired from sulphide minerals, carbon dioxide, oxygen, and air. This water-rock interaction subsequently releases phosphate (Kaur *et al.*, 2018). The microbial activity is thus responsible for the enhancement and largest contributor of acid mine drainage (Kaur *et al.*, 2018). Figure 2.2 below illustrates the sources of pollution during the mining activity as adopted by Kaur *et al.*, 2018. The pollutants generated at mining sites that cause AMD are known as risks that potentially contaminate surface and groundwater (Murarescu *et al.*, 2022). These risks are potentially hazardous and therefore entail the three basic components of risk (described below).

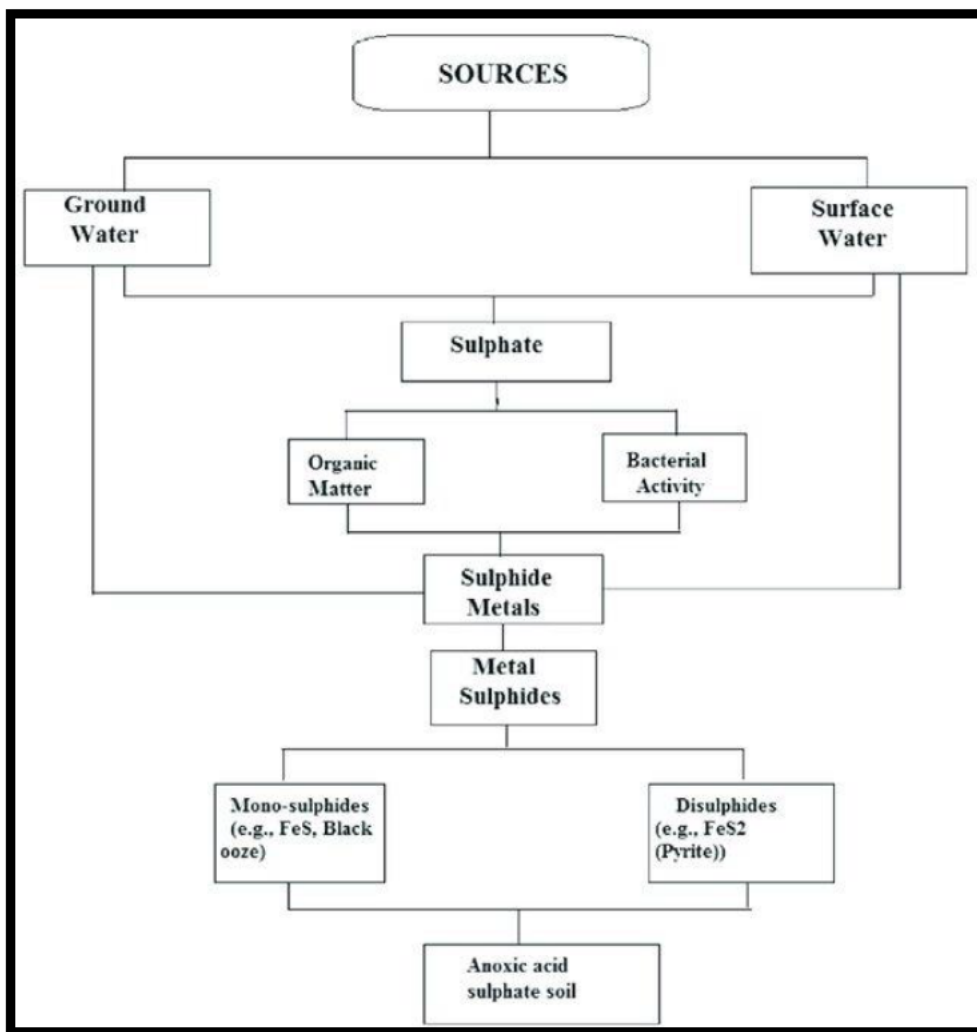


Figure 2.2. Pollutants generated during mining cause acid mine drainage (Adopted from Kaur *et al.*, 2018).

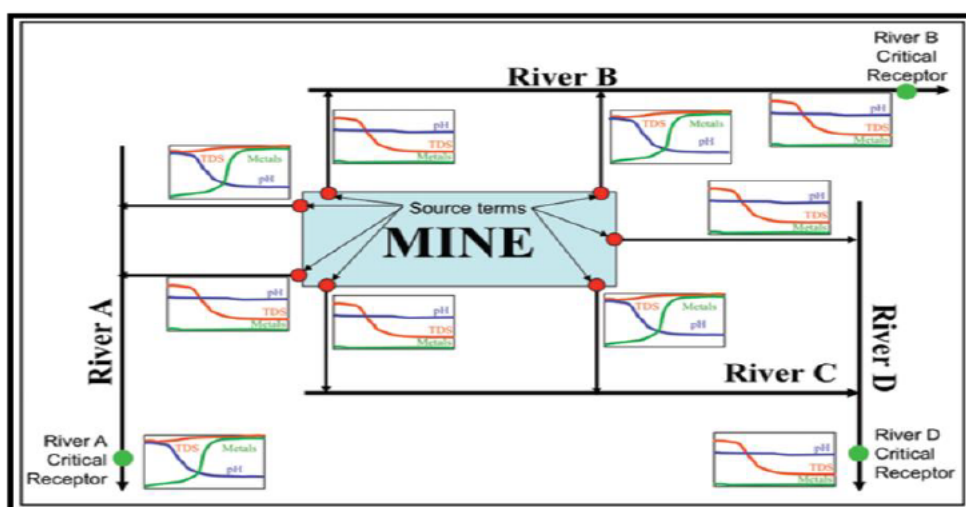


Figure 2.3. Multiple source terms and receptors (Adopted from DWAF, 2008).

The components are the source of the risk, the pathway along which the risk spreads/travels and specific targets known as the receptors that are impacted (DWAF, 2008) Whilst a single source, pathway and receptors are projected for generality, this is unrealistic in the mining fraternity. Figure 2.3 above illustrates multiple source terms, pathways, and receptors in a mining site. This forms a realistic approach to understanding the impacts from source pathway and receptors (DWAF, 2008; GUARD guide, 2014).

2.9 Generation of Acid Mine Drainage

The generation of acid mine drainage in active and abandoned coal mines is due to the sulphide minerals being oxidized when in contact with air, water, and microbial activity (Yuan *et al.*, 2022). The oxidation process does not produce acidity immediately (Villeneuve *et al.*, 2009; Elghali *et al.*, 2023). The production of acid is after lengthy period which is controlled by the reactivity of the sulphides and neutralizing minerals (Bouzahzah *et al.*, 2015; Elghali *et al.*, 2023). The acidity levels and metal composition are dependent on the exposed rock. This determines the acid-producing and neutralisation minerals (Skousen, 2017; Skousen *et al.*, 2019). AMD is thus dependent on the pyrite reserves, which determine the capacity of the acid generation (Wang *et al.*, 2021). Subsequently, when the capacity of acid production surpasses the neutralisation and digestion of minerals that are alkaline, pH will continue to decrease, in addition, metal ions will continue to increase when the dissolved heavy metals exceed the absorption of minerals that are viscous (Wang *et al.*, 2021; Yuan *et al.*, 2022). Consequently, the carbonate and sulphide minerals thus determine the geochemistry of the mine drainage (Elghali *et al.*, 2023). The various types of drainage and characteristics are described in Table 2.1 below.

Table 2.1. Types of drainage produced by sulphide oxidation and their characteristics (Guard GUIDE, 2014).

Acid mine drainage	Neutral mine drainage	Saline mine drainage
pH is acidic	Neutral to alkaline pH.	Neutral to alkaline pH.
Metal concentrations are medium to high.	Low to medium concentration of metals. May contain elevated levels of arsenic, antimony cadmium, manganese, selenium zinc.	Metal concentrations are low, and iron concentrations are moderate.
Sulphate concentration is high	Sulphate concentration low to medium	Moderate concentration of calcium, magnesium and sulphate
Treatment for acid neutralisation, sulphate and metal removal.	Treatment for metal and occasionally sulphate removal.	Sulphate treatment and occasionally metal removal.

2.10 Acid Mine drainage formation and chemistry

Acid mine drainage formation is from the oxidation of pyrite (FeS_2) a common sulphide mineral (Allen *et al.*, 1996; Dold, 2010; Nordstrom, 2011, Dold, 2014) including other sulphides such as galena, sphalerite, chalcopyrite (Lottermoser, 2007) and bornite, molybdenite, arsenopyrite, enargite, and others (Dold, 2014). Iron (Fe^{2+}), and aluminium (Al) are important cations, whilst sulphate (SO_4^{2-}) is the anion (Nordstrom, 2011). The oxidation of the sulphide mineral is further accelerated by microbial catalysis of the oxidation of the aqueous ferrous iron and sulphide (Nordstrom *et al.*, 2015). In addition, when the chemical reactions are linked with evaporation, extremely acidic drainage and very high concentrations of dissolved constituents are experienced (Nordstrom *et al.*, 2015). The pH can range from – 3.5 to 5, however, the chemistry and microbiology involved in the oxidation process and the formation AMD is a complex topic that is still undergoing research (Nordstrom, 2011). Méndez-García *et al.* (2015), indicated that AMD microbial communities are formed due to primary environmental factors such as temperature, total organic carbon (TOC), dissolved oxygen (DO), pH, dissolved metal concentrations and other solutes. Figure 2.4 below illustrates the AMD impact on the environment.

Tan *et al.* (2009); Kuang *et al.* (2013); and Méndez-García *et al.* (2015), note that pH plays an integral role among AMD sites regarding beta-diversity prokaryotic variations as compared to its geographic location. On the other hand, the factors shaping composition of prokaryotic communities is led by dissolved oxygen for biofilm and microbial growths (Mueller *et al.*, 2011; Mendez-Garcia *et al.*, 2014).

The following phyla *Acidobacteria*, *Firmicutes*, *Actinobacteria*, *Nitrospirae*, and *Proteobacteria* are associated with bacteria that inhabit AMD environments (Mendez-Garcia *et al.*, 2014). Others include *Bacteroidetes* that have been detected anecdotally. The phyla *Proteobacteria* are further widely distributed in the acidic ecosystem notably *Acidithiobacillus* spp. (Mendez-Garcia *et al.*, 2014). Subsequently, AMD-related biota is present in niches without well-established boundaries and thrive in microenvironments such as AMD bed sediment, water, and microbial macroscopic growths, which are present in ~ 30% of AMD sites characterised globally (Méndez-García *et al.*, 2014).

This complex chemistry is highly variable containing numerous reactions of secondary minerals that form in AMD and other rock environments for sulphide mineral chemistry (Pope *et al.*, 2010). Therefore, minerals, such as carbonates, will mitigate AMD due to its neutralising

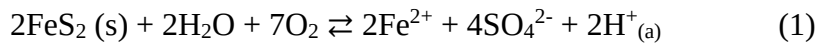
capacity; subsequently the chemistry of acid neutralising and acid forming minerals is dependent on its relative reactivity and abundance within specified geological, hydrological, and environmental conditions. (Pope *et al.*, 2010).

Pope *et al.* (2010); Dold, (2010) and others indicate pyrite oxidation in the formation of acid mine drainage takes place at several significant chemical steps. However, the three (3) major steps in this process are catalysed chemically or biologically, including partially oxidised sulphur (S) species as well as transient complex iron (Fe) ions, and involve several secondary minerals. They are as follows:

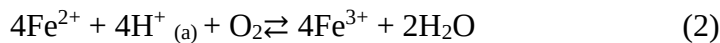
- The oxidation of reduced sulphur (S) to sulphate (SO_4^{2-}) (Equation. 1 below),
- The oxidation of Fe (II) to Fe (III) (Equation. 2 below, acid-consuming reaction), and
- The hydrolysis of Fe (III) to precipitate ferrihydrite, $\text{Fe}(\text{OH})_3$ (Equation 3 below).

The pyrite consumption ratio to acid formed remains the same for the complete oxidation/hydrolysis process (Pope *et al.*, 2010; Dold, 2010).

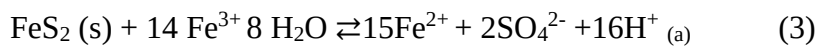
Banks *et al.* (1997), explain this complex reaction as follows:



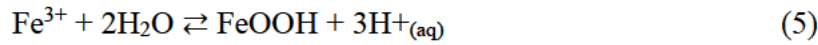
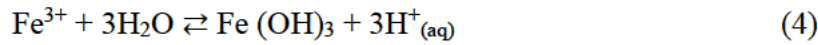
(Pyrite + oxygen + water = ferrous iron +sulphate +acid)



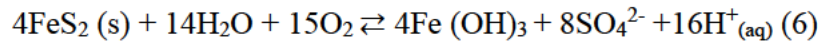
In equation 2 above partial oxidation of ferrous (Fe^{2+}) to ferric iron (Fe^{3+}) consumes some protons. Microbial activity accelerates this chemical reaction rate (e.g., Acid thiobacillus spp. or Leptospiral spp.) (Dold, 2014). Further pyrite oxidation or hydrolysis may occur due to the ferric ion acting as an electron acceptor (Banks *et al.*, 1997). Both these processes further release protons as illustrated below.



Sharma *et al.* (2020), indicate the Fe (III) precipitates are referred to as “**yellowboy**”. This occurs as the pH increases, and dissolved iron concentration decreases. Hence the solubility of Fe^{3+} is limited by the precipitation of Fe^{3+} hydroxides [$\text{Fe}(\text{OH})_3$] and oxy-hydroxides (FeOOH). Subsequently an increase in pH of more than 3 triggers reactions 4 and 5 below, (Prabhakar and Lottermoser, 2015)



Stumm and Morgan (1996); Banks *et al.* (1996); Weber *et al.* (2004); Dold (2014); Sharma *et al.* (2020); and others demonstrate the overall sequence of reactions below as acid-producing:



(Pyrite + Oxygen + Water $\rightleftharpoons$ Iron Hydroxide + Sulphuric Acid)

Dold, (2014) further explains this net reaction of pyrite oxidation being the most efficient producer of acid among the common sulphide minerals. The main acid producer is hydrolysis of $\text{Fe}(\text{OH})_3$ and varying amounts of protons, metals and other harmful elements/compounds are released to the environment.

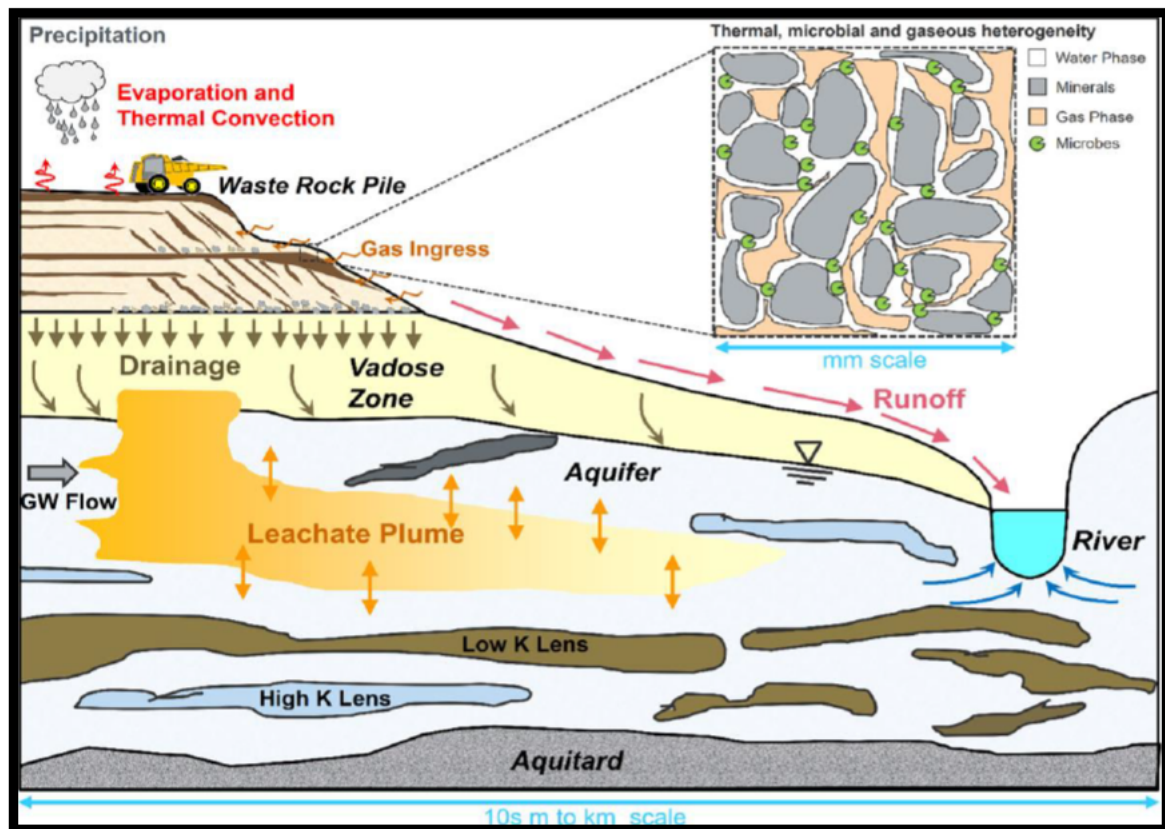


Figure 2.4. Schematic diagram illustrating AMD and the leachate from the waste rock dump into the environment impact surface and groundwater (Adopted from Muniruzzaman and Pedretti, 2020).

2.11 Acid mine drainage minerals

The minerals Pyrite (FeS_2) and pyrrhotite [$\text{Fe}(1-x)\text{S}$] are formed during the oxidation process (Dold, 2014) occurring via biological and inorganic pathways (Parbhakar-Fox and Lottermoser, 2015) and is well documented in the literature for the production of acid mine drainage (Banks *et al.*, 1997; Pope *et al.*, 2010; Nordstrom *et al.*, 2015), however there are different sulphide minerals as per different ore deposits. Pyrite remains the dominant sulphide mineral responsible for acidic generation, (GARD Guide, 2009). Iron sulphides with molar/metal ratio <1 such as pyrite, marcasite and pyrrhotite and sulfosalts such as enargite generate acid when they react with water. Sulphides such as sphalerite, galena, and chalcopyrite with metal/sulphide ratios = 1 does not generate acidity when oxygen is the oxidant. (GARD Guide, 2009). Subsequently, as a result of pyrite oxidation several meta-stable secondary minerals are formed depending on the geochemical conditions. The metal stable minerals respectively include schwertmannite, (between $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$ and $\text{Fe}_{16}\text{O}_{16}(\text{OH})_{10}(\text{SO}_4)_3$, ferrihydrite $5(\text{Fe}^{2+}\text{O}_3 \cdot 9\text{H}_2\text{O})$ and goethite ($\text{FeO}(\text{OH})$). The stable secondary minerals include jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) and hematite (Fe_2O_3). Other sulphide minerals include stibnite, argentite, and stannite (Pat-Espadas, *et al.*, 2018).

2.12 Acid Mine Drainage Prediction

Acid mine drainage prediction is currently the principal environmental issue facing the mining industry. Accordingly, accurate mine waste characterisation is required for the evaluation of the geochemical stability and prediction of future impacts with timely mitigation. (Dold, 2017). This will ensure accurate assessments of risks are documented and waste management classification programmes/schemes are designed and implemented (Prabhakar-Fox and Lottermoser, 2015).

“The term Acid/Base Account means different things to different people. Some use the acid/base account (ABA) to evaluate the suitability of overburdened materials for mine soils, while others use the ABA to predict post-mining water quality.” (Hossner and Brandt., 1997). The latter was adopted for this study to predict the water quality post mining from an existing abandoned coal mine dump.

ABA is an analytical investigation procedure that was first developed in the 1960s by West Virginia University Scientists. Further reviews of this method were undertaken during the late 1960's and 1970's (Smith, *et al.*, 1976; Abfertiawan *et al.*, 2023). Subsequently, in 1978, the methods applicable to mine soils and overburdens were globally adopted to determine potential

acid generation (Sobek, *et al.*, 2000). This analytical method assesses the acid-producing and acid-neutralising potential of overburdened rocks prior to mining and has thus become a preferred method for predicting post-mining water quality and prediction of the water quality at mining sites (Skousen *et al.*, 2002).

International standard practices have evolved into the adoption of the ‘Wheel Approach’ for the prediction of drainage chemistry (Morin and Hutt, 1998). This approach ensures that all tests are conducted as reflected in Figure 2.6 and compared to ensure accurate prediction of metal leaching and acid mine drainage (Morin and Hutt, 1998). The two extensive methods used for acid mine drainage assessment and characterisation are the static and kinetic tests. (White *et al.*, 1997; Smart *et al.*, 2002; AMIRA, A., 2002). The static laboratory tests involving a single measurement are referred to as acid-base account (ABA) and the net acid generation (NAG) test. This test determines the potential for acidic and neutral drainage from the sulphide and carbonate minerals present in the sample (Smart *et al.*, 2002). These tests include the following electrical conductivity (EC) and pH test, determination of total sulphur and total carbon, acid neutralising capacity (ANC) test, net acid-producing potential (NAPP) calculation (ANC and S), net acid generation (NAG) test (includes kinetic NAG and Sequential NAG) (Smart *et al.*, 2002). On the contrary, the kinetic test (long term) determines the rate of acid generation, sulphide reactivity, oxidation kinetics and metal solubility (AMIRA, 2002; Smart *et al.*, 2002; Abfertiawan *et al.*, 2023). The kinetic tests include the laboratory column, humidity cell and field-based pad tests. (Morin and Hutt, 1998). The free-draining column leach test methodology has been well-documented, explained and reviewed by numerous authors (Prabhakar-Fox and Lottermoser, 2015; White *et al.*, 1999). The static and kinetic test methods adopted for this project are explained in detail in the research methodology, chapter 4 of this thesis. Figure 2.5 illustrates the process adopted for the prediction and classification of the samples for this study. Table 2.2.1 to 2.2.3 below briefly overviews the advantages and disadvantages of geochemical testing for acid mine drainage.

A comprehensive study by Parbhakar-Fox and Lottermoser, (2015) conducted on the acid mine drainage prediction methods and practices highlights the advantages and limitations (Table 2.3.1) of the current geochemical methodology adopted for acid mine drainage. Parbhakar-Fox and Lottermoser, (2015) indicated that the future of acid mine prediction lies in the reinventing the wheel approach done by Morrin and Hutt (1998), as presently the global mining industry relies on the geochemical methodology that was established in the 1970’s. This methodology

is associated with many limitations and has the potential to over or underestimate the acidic forming potential through the use of aggressive tests such as Sobek test and sequential NAG test (Parbhakar-Fox and Lottermoser, 2015).

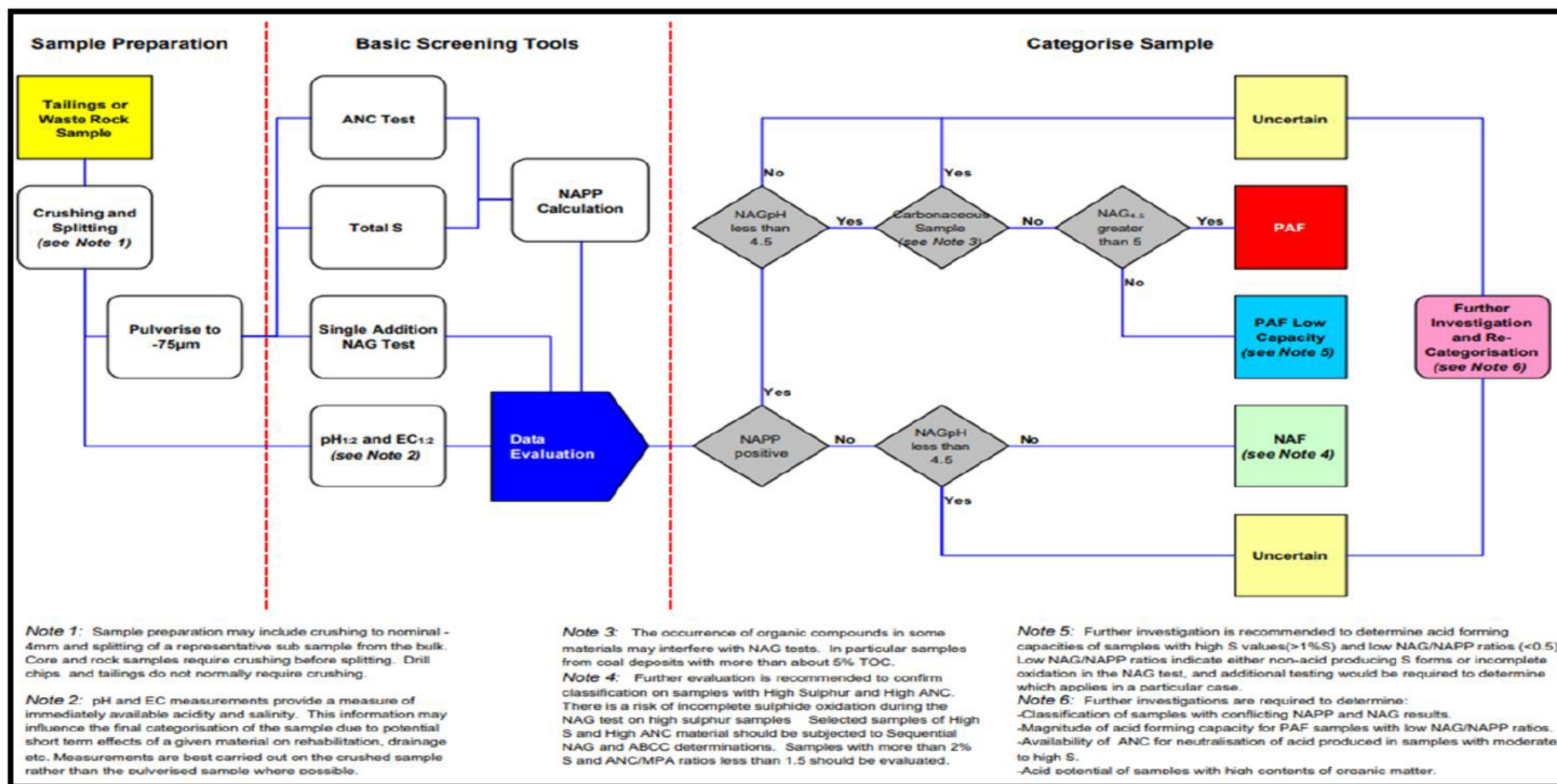


Figure 2. 5. Acid mine drainage flow chart indicating sample preparation, screening, decision nodes, and classification of the sample (Adopted from AMIRA, 2002).

Further to this, the calculation NAPP using total sulphur as compared to using sulphide sulphur has the potential to over or underestimate the acidic potential (Parbhakar-Fox and Lottermoser, (2015). Special attention needs to be given to the acid mine drainage forming minerals (e.g. jarosite) and silicate neutralizers (e.g. chlorite), as this is limited by the current methodology.

The current established protocols in the wheel approach do not appropriately characterise fundamental aspects of AMD such as microbial processes, mineralogy, and texture. Regardless of the limitations experienced, the AMD tests and protocol are extensively used (Parbhakar-Fox and Lottermoser, (2015).

2.13 Legislation of water resources protection, and management in South Africa

In South Africa, water resource management and protection are guided by the following legislation, Constitution of the Republic of South Africa (Act 108 of 1998), National Water Act (Act 36 of 1998) and the Water Services Act (108 of 1997). Further to this the National Water Resource Strategy 3 provides a framework for the management and control of water resources, protection, development, use and conservation. The strategy also provides a framework within which water management is conducted regionally or at a catchment level.

With respect to the mining sector, water management is guided National Water Act, Mineral and Petroleum Resource Development Act 28 of 2002 and the National Environmental Management Act (Act 107 of 1998). The above legislative measures ensure water resource protection across all water use sectors to enable equitable sustainable growth and ecosystem functioning for the benefit of current and future generations (DWS, 2023).

Table 2.2.1. Prediction techniques, advantages, and limitations (Parbhakar-Fox and Lottermoser, 2015).

Technique	Test	Principle	Description	Advantages	Limitations
Geo-environmental deposit modelling	Desk-study during early life of mine stages	Information on environmental characteristics of a deposit	Empirical models evaluate and rank ore deposit properties in ARD terms	- Highlights potential environmental problems that arise from the unique geological attributes specific to a deposit type - Allows for early forecasting of potential liabilities and identification of appropriate rehabilitation options	- Qualitative descriptions - Too many assumptions made on ARD controls - Bias of current models to North American sites - Current published models are either too site specific, or too general
Sampling strategies		Determination of appropriate sample numbers to use in ARD prediction testwork	General guidelines for number of samples based on stage of operations or deposit mass	Early apportioning of funds to finance the predictive campaign permitted through early identification of the minimum sample number required	- No global standard procedure for sampling - Sample selection may be non-systematic, can result in bias sampling
Short-term field tests	Drill core evaluation	Visual inspection of acid forming/neutralising minerals	Environmental logging of intact drill core by codes such as the acid rock drainage index	Cost effective deposit-wide evaluation of ARD forming characteristics on intact samples	- Subjective - Additional time added to geological logging
	Paste pH	Measurement of current acid forming characteristics	Water added to powdered or crushed sample, pH measured after a period of time	Rapid indication of leachable acidity, resulting data can be used as part of ARD domaining	- Not a predictive test - No global protocol standard exists
	USCS Field leach test	Measurement of soluble metals	Water added to sieved sample, solution analysed for dissolved metals	Fast, simple, and cost-effective, can be performed in the field with no specialist equipment required	Not a predictive test
	Wall washing	Characterisation of ARD/ML potential of in-situ rock	Measurement stations constructed on exposed rock surface, rinsed with deionised water, and leachate analysed	- In-situ ARD prediction - Results can support modelling of future mine water quality	- Complex experimental setup - Infrequent sampling does not permit an understanding of net chemical changes
	Total metals	Quantitative assessment of metals and metalloids	XRF, ICP or portable XRF (pXRF) analyses	Quantitative data of total metals and metalloids	- XRF and ICP analyses are costly and can have long turnaround times - pXRF data acquisition needs to be accurate and precise
Static tests	Carbon	Assessment of acid neutralising capacity (ANC)	C_{Total} , $C_{Organic}$ and $C_{Inorganic}$ determined by sample pretreatment, high-T combustion, and infrared spectrometry	Relatively simple and low-cost	- Inefficient procedure to determine $C_{Inorganic}$ - Some carbonate minerals do not contribute to ANC - Net carbon value (NCV) methodology is not widely used
	Sulphur	Assessment of maximum potential acidity (MPA)	S_{Total} , $S_{Sulphide}$ and $S_{Sulphate}$ determined by sample pretreatment, high-T combustion, and infrared spectrometry	- Simple to measure - Occasionally, data collected by routine S assay for other mine-site disciplines	MPA based on S_{Total} can lead to overestimation if not acid forming minerals (e.g., barite, gypsum; non-Fe bearing sulphides) are present

Table 2.2.2. Prediction techniques, advantages, and limitations (Adopted from Parbhakar-Fox and Lottermoser, 2015).

Technique	Test	Principle	Description	Advantages	Limitations
Kinetic tests	Acid base accounting (ABA)	Calculation of Net-Acid Producing Potential (NAPP = MPA-ANC) or Neutralisation Potential Ratio (NPR = ANC/MPA)	• MPA calculated based on S_{Total} or $S_{Sulphide}$ • ANC determined by laboratory titration methods	• Industry-wide practice, with commercial laboratories offering this testing, therefore results are easy to understand and interpret	• MPA overestimated if based on S_{Total} • MPA and ANC tests are not performed on exactly the same sample material • ABA procedure is not standardised, site-by-site comparisons are not possible • Organic matter interferes with measurements • H_2O_2 quality must be ensured • Calcite and dolomite may react during NAG testing, $Ca(OH)_2$ and alkaline pH values result • Interpretation of results is cumbersome and not standardised
	Net Acid Generation (NAG) test	Determination of acid forming potential capacity	Addition of H_2O_2	• Industry-wide practice • NAGpH versus NAPP geochemical plots routinely used for waste classification	• Organic matter interferes with measurements • H_2O_2 quality must be ensured • Calcite and dolomite may react during NAG testing, $Ca(OH)_2$ and alkaline pH values result • Interpretation of results is cumbersome and not standardised
	Acid buffering characteristic curve (ABCC) test	Measurement of acid neutralising capacity	HCl titration	• Only measures the effective acid neutralising portion	• Interpretation of results is cumbersome and not standardised
	Leachable metals	Synthetic precipitation leach procedure (SPLP method 1312)	Partial leach	• Screening-tool for leachable metals	• Inappropriate in replicating a natural environment with regards to extracting fluid concentration and pH
	Biological acid production potential testing	Assessment of sulphide oxidising bacteria on ARD formation rate (ASTM E1915-11)	Bacterial partial leach	• Allows for biological contribution of acid forming bacteria to be measured in a practical manner	• Technically challenging • Not an appropriate screening tool • Role of other ARD-forming bacteria not considered
	Humidity cell tests	Mimics weathering of waste rock, with leachate chemistry assessed	ASTM D5744 method	• More realistic indication of leachable metals/metalloids than short-term SPLP tests • Attempts to mimic climatic cycle	• Mineral precipitation does reflect actual mine site conditions • Day 7 rinse may remove all reaction products • Equilibrium conditions not reached due to short contact times • No integration of mineralogical and microtextural analyses
	Column leach tests		AMIRA P387A method	• More realistic indication of leachable metals/metalloids than short-term SPLP tests • Procedural flexibility • Low maintenance	• Unrealistic replication of climatic conditions
	Field test methods	Monitor leachate quality of waste rock directly under natural conditions	Tubs, barrels or test piles of wastes left to weather under natural conditions	• Exposure to site-relevant climatic and microbiological conditions	• No integration of mineralogical and microtextural analyses • Not standardised • Larger scale piles expensive to construct and maintain
	Optical microscopy	Identification of acid forming and neutralising minerals	Sulphide alteration index (SAI) and acid rock drainage index (ARDI) proposed	• Examination of sulphide and carbonate textures	• Not standardised • Technically challenging • Subjective • Not statistically valid
	Bulk mineralogy	Quantification of acid forming and neutralising minerals	X-ray diffractometry (XRD)	• Quantitative mineralogy • Data can be used for MPA/ANC calculations	• Expensive • Detection limits • Identification of trace phases impossible
Mineralogical characterisation					

Table 2.2.3. Prediction techniques, advantages, and limitations (Adopted from Parbhakar-Fox and Lottermoser, 2015).

Technique	Test	Principle	Description	Advantages	Limitations
	Automated mineralogy	Classification of intact mineralogy	Mineral liberation analyser (MLA) and Quantitative Evaluation of Minerals by SCANning electron microscopy (QEMSCAN)	• Data collection procedures well established • Negligible error margin with offline post-processing allowed • Ability to utilise data collected as part of other resource characterisation works	• No guidelines for ARD relevant data collection or processing • Technically challenging • Expensive

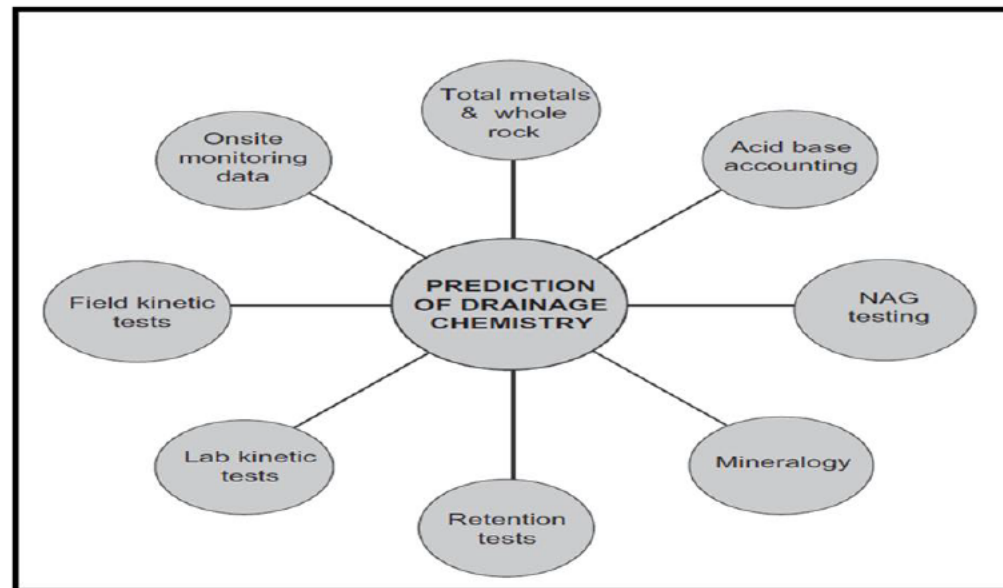


Figure 2. 6. The prediction of drainage chemistry, Wheel approach (Adopted from Morin and Hutt, 1998).

Table 2.3.1. Static and kinetic testing advantages and disadvantages (Adopted from Lottermoser, B., 2015).

Geochemical Testing	Advantages	Disadvantages
Static testing	Tests are rapid and conducted over hours and days	Does not consider microbial activity and actual particle size on site.
	Low-cost tests to evaluate the net acid potential	Disregard different dissolution rates of individual minerals and associated acid production and consumption
		The dissimilarity between actual site conditions and laboratory testing and
Kinetic testing	Confirms static testing	Dedicated laboratory/field space, skilled laboratory technician's evaluators and time are required.
	Recognise dominant weathering reactions	Equipment configuration and experimental conditions used, for example, (e.g.) waste grain size which may not be representative of the sample.
	Establish acid formation rates and assess AMD potential	Data cannot accurately provide actual water quality for the future
	Determination of the potential of the acid generation to occur	Long-term kinetic tests preclude their use from mine pre-feasibility and feasibility studies
	Forecast chemical composition and temporal variations in leachate quality	
	Estimate the release rate of compounds and elements from the tested material.	

2.14 Conclusion

This chapter highlighted an in-depth literature survey on the holistic issue concerning the generation of AMD, sources, chemistry, and prediction, Subsequently, the protection of water resources from heavy metal pollution that emanates from abandoned coal mines and discarded dumps necessitates urgent intervention from government, civil society, and the private sector.

This collective approach will aid in the protection of the water resources with respect to surface and ground mine water management. Morin and Hutt (2006) also emphasise that a significant cost factor in mining operations pertains to the long-term management and treatment of water resources. This is attributed to the presence of acidic pH and/or elevated aqueous metal concentrations, which necessitate extensive and ongoing attention. Successful mine water management programmes from abandoned coal mines and coal discard dumps can be achieved with correct quantification of the acidic mine drainage occurrence, rates, and impacts into the water resources.

CHAPTER THREE

REGIONAL SETTING / STUDY AREA

3.1 Introduction

This chapter details the regional physiographical characteristics (geology, drainage, topography, climate, vegetation, bird, mammal, reptile, and other life) and sampling sites of the coal discard dump and water resources within the study area. Surface water quality sampling of two watercourses (Biggarsgatspruit and Wasbank River) and coal discard sampling for geochemical characterisation of a coal discard dump (Indumeni coal mine dump) is further illustrated. This coal mine discard dump has been in existence since pre-1965 (more than 56 years old) during the operational phase and post-closure of the mine in 1986.

3.2 Regional Description

3.2.1 Study Area

The area is located within the coal fields of South Africa in the northern part of the KwaZulu-Natal Province (Figure 3.1). Specifically, the site is located close to the town of Wasbank which, in turn, is located within the uMzinyathi District (DC24) and the Endumeni Local Municipality (Figure 3.2). The uMzinyathi District Municipality is located within the uThukela Water Management Area (Sandspruit Catchment-V Catchment Drainage region) in KwaZulu-Natal (UDM, 2016). It comprises four local municipalities, of which the Endumeni Local Municipality is the smallest in terms of extent (1610 km²) and population size. The Biggarsberg Valley is located within the Endumeni Local Municipality (ELM, 2016) (Figure 3.2).

The local municipality is 290 km from Durban and 360 km from Johannesburg (UDM, 2016 and ELM 2016). There are three towns within this municipality, all of which have well-established road, rail, and infrastructure network (UDM, 2016). The towns are Dundee (a historical battlefield area and now tourist attraction), Glencoe and Wasbank (the latter a small town at the base of Endumeni Mountain). Water is a scarce resource in the region, but the towns of Dundee and Glencoe have a constant supply drawn from six dams constructed on the uMzinyathi/Buffalo River, thus making the Endumeni Municipality region a development hub of northern KwaZulu-Natal (UDM, 2016). Mining forms part of major economic sector within the municipality attributing 1.47%. The other sectors include farming; social services, trade,

manufacturing, business serves, private household/domestic workers, business services; transport, construction; mining; and utilities (UDM, 2016).

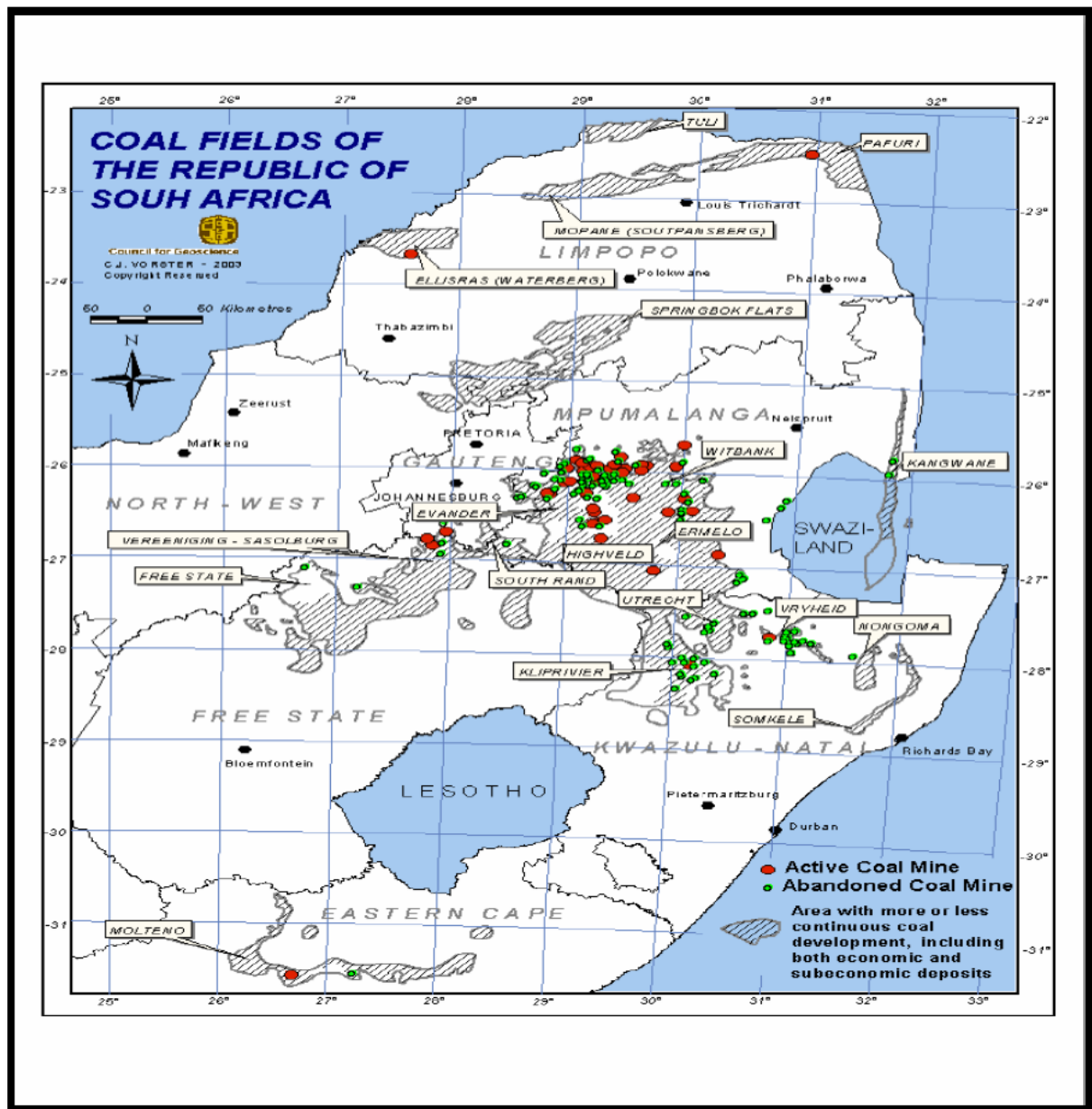


Figure 3. 1. Coal fields of SA illustrating the active and abandoned mines in South Africa (C.J. Vorster, 2003) in Schmidt, 2010.

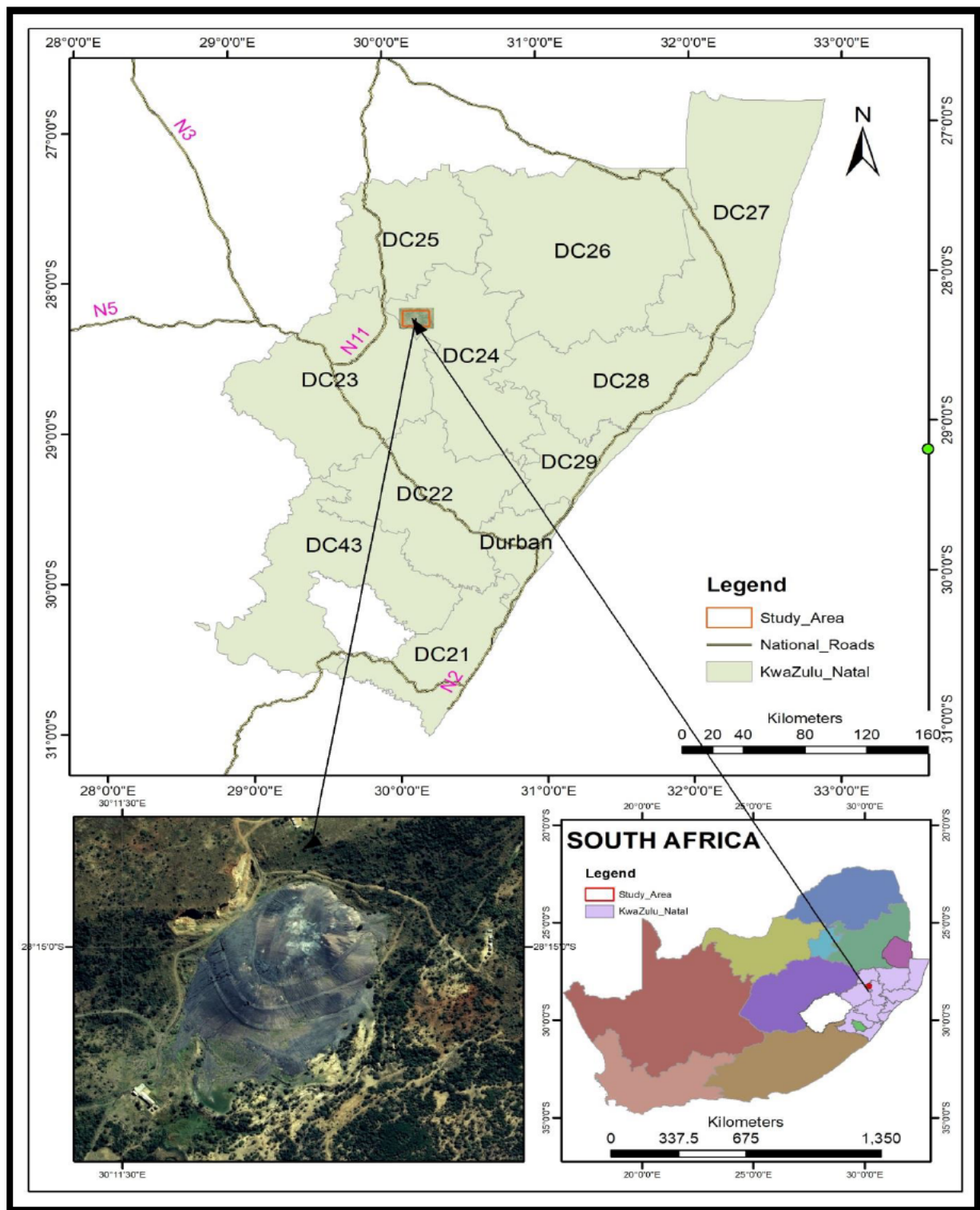


Figure 3. 2. Location of the Indumeni Discard Dump Site within the uMzinyathi District Municipality (DC24 on the map), within the KwaZulu-Natal Province of South Africa.

3.2.2 Location of Study Area

The Klip River Coal field (Figure 3.1) is the largest of the three geographically distinct coal fields in northern Natal. (Anhaeusser and Maske, 1986). The coal field is bounded by the eastern escarpment of the Drakensburg plateau from north to south (Anhaeusser and Maske, 1986) within the uThukela Water Management Area (Hancox and Götz, 2014).

The Indumeni coal discard dump and surrounding areas inclusive of affected watercourses (Figure 3.3 and Figure 3.4 respectively) is located within the Klip River Coalfields close to the town of Wasbank. Access to the coal discard dump property is via the Victoria Road exiting the town of Dundee. Access to the actual coal discard dump is via an unnamed corrugated farm road. Global positioning coordinates to the dump is 28° 15' 16.7" S and 30° 11' 33.0" E.

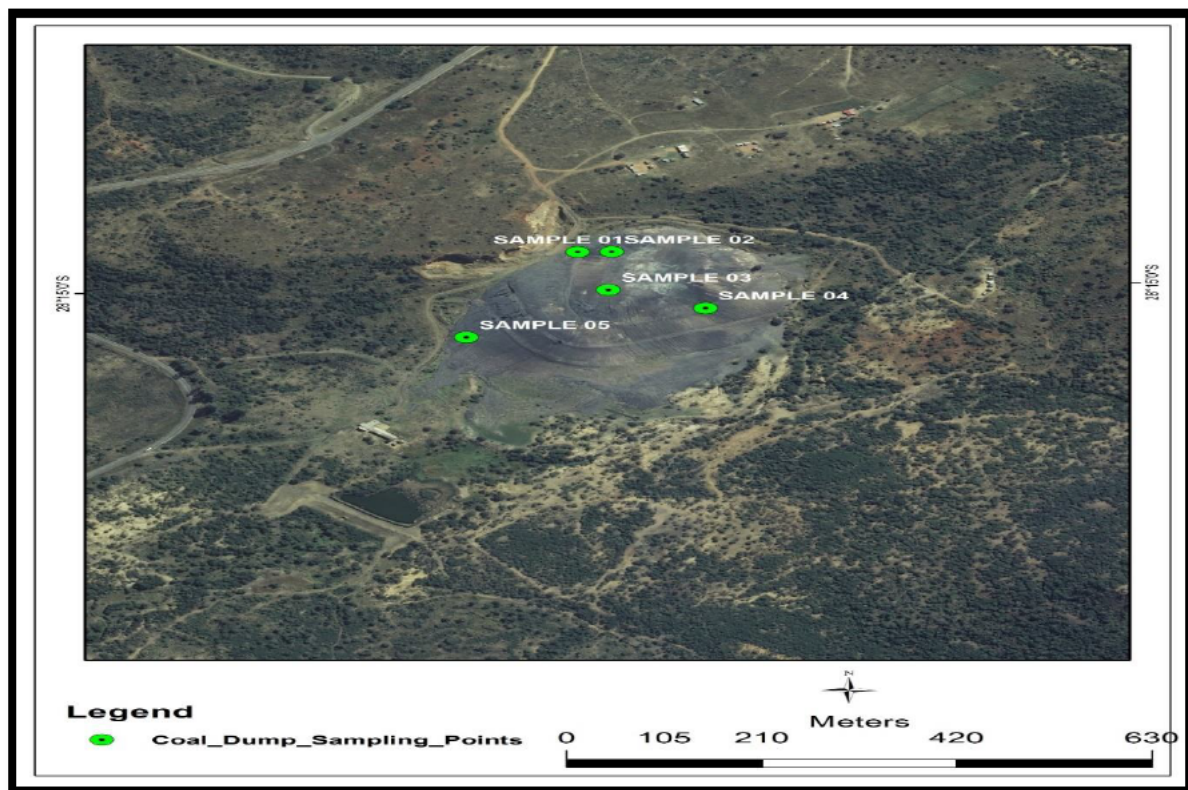


Figure 3. 3. The study area indicating coal discard sampling sites on the Indumeni coal discard dump. (Source: Google Earth®).

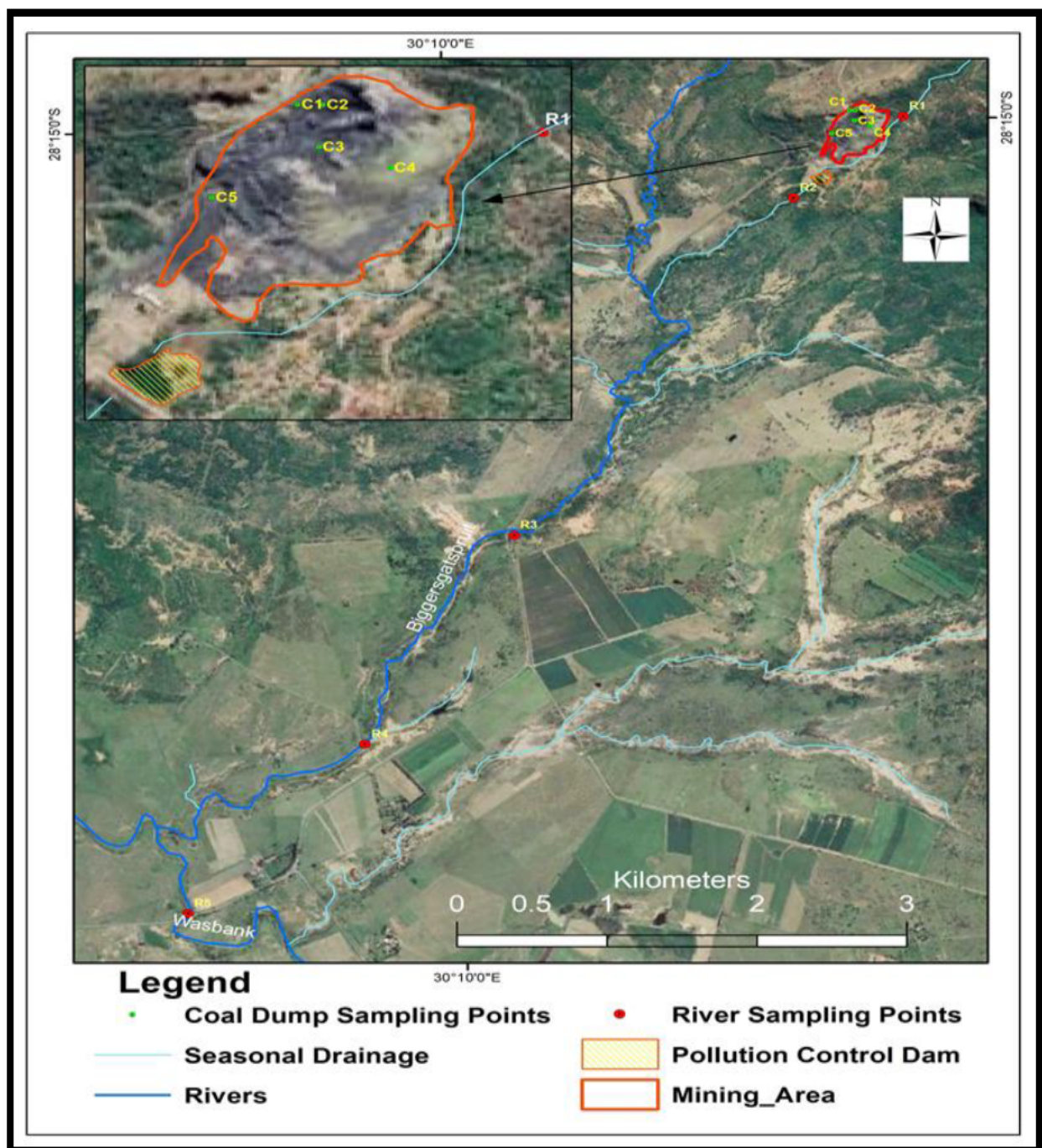


Figure 3.4. The study area indicating the 5 water resource sampling sites on the Biggarsgatspruit and Wasbank River and the 5-coal discard sampling points on the discard dump.

In 1996 a spring (or as is locally known: ‘pop-up’) developed at this colliery discharging highly polluted water from the underground workings into the watercourses. The impacted water has since been diverted into a pollution control dam (constructed by the then Department of Water

Affairs and Forestry) on the southern side of the coal discard dump prior to being discharged into the Biggarsgatspruit, a tributary of the Wasbank River. The Wasbank River flows into the Sundays River, and latter into the Tugela River which eventually flows into the Indian Ocean via the Tugela Estuary. Figure 3.3 indicates the 5 coal discard sampling points on the actual discard dump and Figure 3.4 indicates the 5 water resource sampling points on the Biggarsgatspruit and Wasbank River (sample point 1-Biggarsgatspruit River upstream of the Indumeni decant; sample point 2-Indumeni pop Decant; sample point 4-Biggarsgatspruit stream downstream lower Biggarsgatspruit and Indumeni Decant; sample point 4-Biggarsgatspruit at De Kroon low-level bridge, upstream confluence of the Wasbank River; sample point 5-Wasbank River downstream Biggarsgat stream on Wasbank-Dundee road bridge). The 5 coal discard sampling points and 5 water resource sampling points are illustrated in Figures 3.3, and 3.4 above respectively.

3.2.3. Topography

The topography of KwaZulu Natal is diverse (Ramulifho, *et al.*, 2018) and extensively characterised by valley hills and bushveld, wetlands, deep river gorges, and grasslands. (UMDM, 2019) with a maximum altitude of 3443 meters (Topgraphic-map.com, 2021). Eeley *et al.* (1999), describe the altitude in the east as flat coastal plain over a series of plateaux which reaches over 3000 meters to the Drakensburg mountains. This forms the western boundary of the province. The mountainous western region experiences vast annual variation in both rainfall and temperature whilst the eastern region receives rainfall throughout the year (Eeley *et al.*, 1999).

The town of Wasbank (within the study area) is located at 1069 meters above sea level (masl) (FloodMap.net, 2021). As per Figure 3.6 below, the discard dump location within the north-eastern part of the town with an undulate mountainous terrain.

3.2.4 Drainage

The research area is within the Eastern Escarpment drainage region of South Africa (Rivers-Moore *et al.*, 2007) and recorded numerous Flagship rivers prioritised for the retention of their natural unique and unimpacted status in South Africa (Driver *et al.*, 2011). The rivers typically exhibit a distinct escarpment zone, and flatter mid-slopes which steepen into eastern coastal zones (Rivers-Moore *et al.*, 2007).

Götz, 2014). The following are named/listed in stratigraphic succession: Dwyka; Eccca; Beaufort and Stormberg-Drakensberg Groups as indicated in Figure 3.7 (the latter containing the Molteno, Elliot and Clarens Formations) (Catuneanu *et al.*, 1998; Hancox and Götz 2014). These formations occupy the Permian of the Karoo Supergroup lithologies, of mudstone; siltstone; sandstone; minor conglomerate and coal outcrop (Catuneanu *et al.*, 2005). These are capped by approximately 1.4 km of basaltic lavas of the Drakensberg Group, the extrusion of which is related to the break-up of the Gondwana Supercontinent (Hancox and Götz 2014).

The geological formation of the study area is part of the Klip River coal field. This is part of the Vryheid formation (Ecca Group) (Figure 3.6) occurring between the Late Carboniferous Dwyka Group and the Late Permian-Middle Triassic Beaufort Group is the Ecca group (Catuneanu *et al.*, 2005). These groups have distinct proximal and distal facies (Hancox, 2016). Sedimentary rocks part of Vryheid Formation represents some of the most distal facies of the Ecca interior seaway (geosynclinal sea) (Green *et al.*, 2012) This was deposited during gradual transformation from marine to non-marine conditions forming extensive coal deposits within a mudstone–sandstone succession (Green *et al.*, 2012).

The Klip River Coalfield comprises of 5 coal seams (Figure 3.8 below), the Top Seam (No. 3 Seam) and the Bottom Seam (No. 2 Seam). In addition, there is an Extra Bottom Seam (No. 1 Seam) (Hancox and Götz, 2014). The seams that have been commercially extractable are the Top Seam and Bottom Seam (Hancox and Götz, 2014), however the commercial viability of the Extra Bottom Seam is yet to be known.

The geological description of the Bottom Seam is equivalent to the Gus Seam. The extent of the seam is 1.3 meters in the north, and 0.5 meters in the south. The Top Seam is more well established than the Bottom Seam and is equivalent to the Alfred Seam. It is 3.3 meters in extent to the north and 1.5 meters in extent in the south (Jeffrey, 2005).

The Top Seam and the Bottom Seam occurs stratigraphically 200 meters above the top of the Pietermaritzburg Formation and 120 meters below the base of the Volksrust Formation (Hancox and Götz, 2014). The seams are separated by between 0.3 and 15 meters of coarse-grained to pebbly, cross-stratified sandstone, which fines upwards into carbonaceous siltstone and mudstone (Hancox and Götz, 2014) as illustrated in Figure 3.8 below.

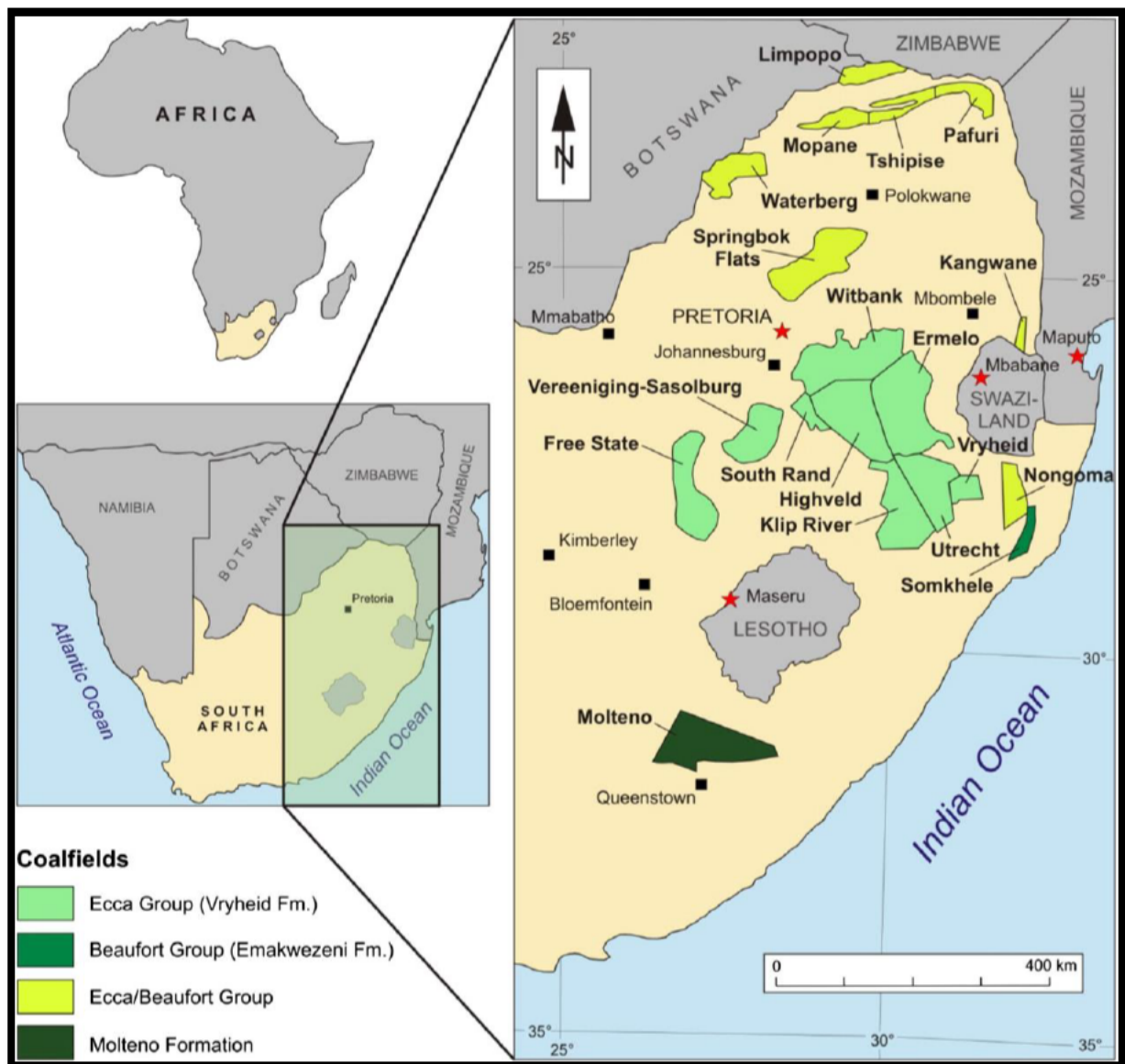


Figure 3.6. Coalfields of South Africa with reference to the Klip River Coal Field modified after Snyman (1998) in Hancox and Götz, (2014).

The Top Seam and Bottom Seam are characterized by increased concentrations of sulphur and phosphorus. In a broad-spectrum, this coal field contains brightly coloured coal that ranges from bituminous to anthracite coal and noted for the production of good cooking coal (Jeffery *et al.*, 2015).

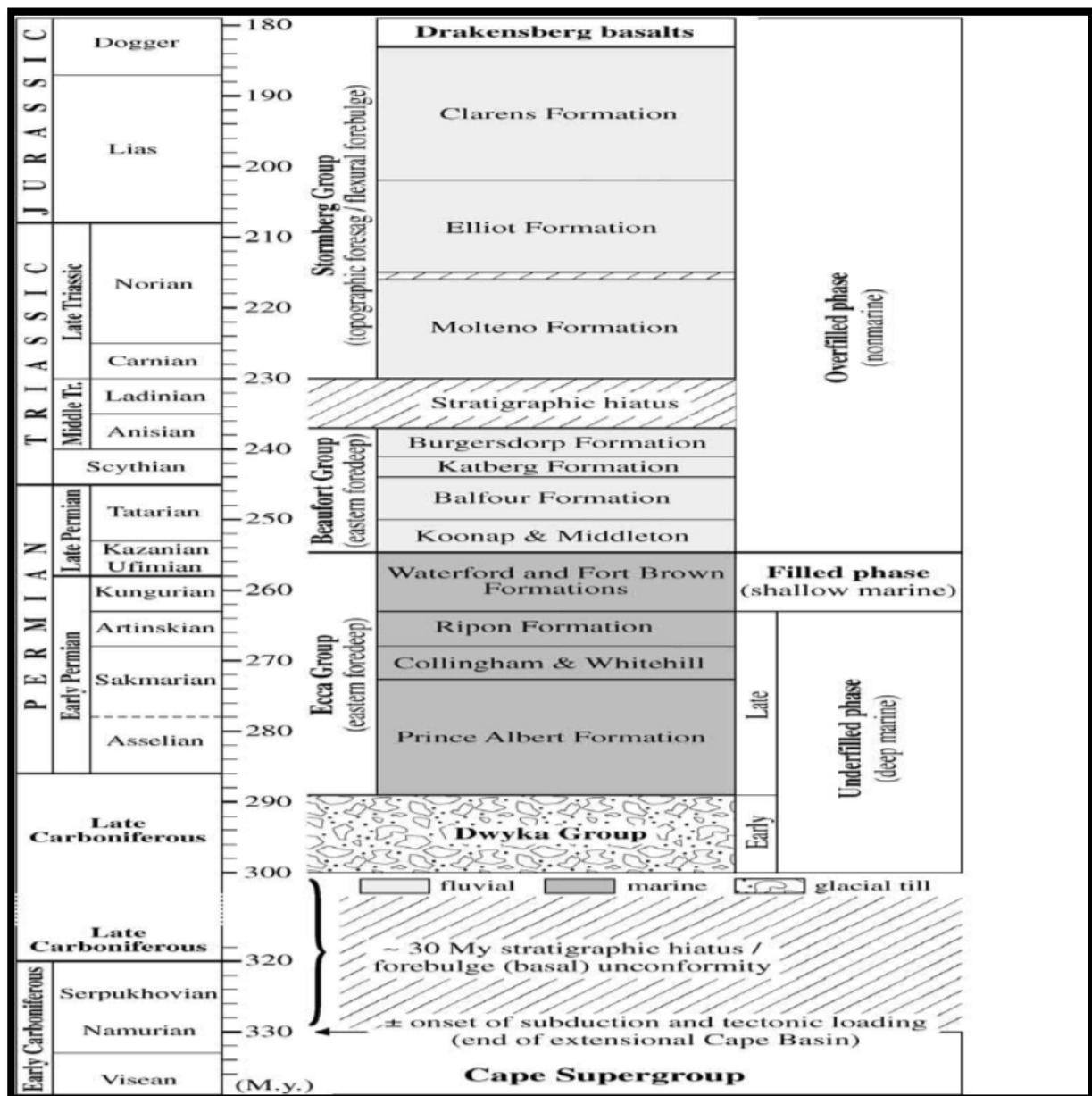


Figure 3. 7. Stratigraphic chart showing major lithostratigraphic subdivisions of the Karoo Supergroup in the main Karoo Basin of South Africa (based on the time scale of Palmer, 1983, and compiling information from Rubidge, 2005 and Catuneanu, 2004a) in Catuneanu *et al.*, 2005.

This Klip River Coal Field is further characterised by 9 dolerite sills, 4 are considered major sills (Zuinguin, Utrecht, Ingogo and Talana) and Dykes (Jeffrey, 2005). The dykes are situated to the northwest-southeast and northeast-southwest of the coalfield (Jeffrey, 2005), arenite and shale are the most common rocks throughout the uMzinyathi District (UDM, 2020).

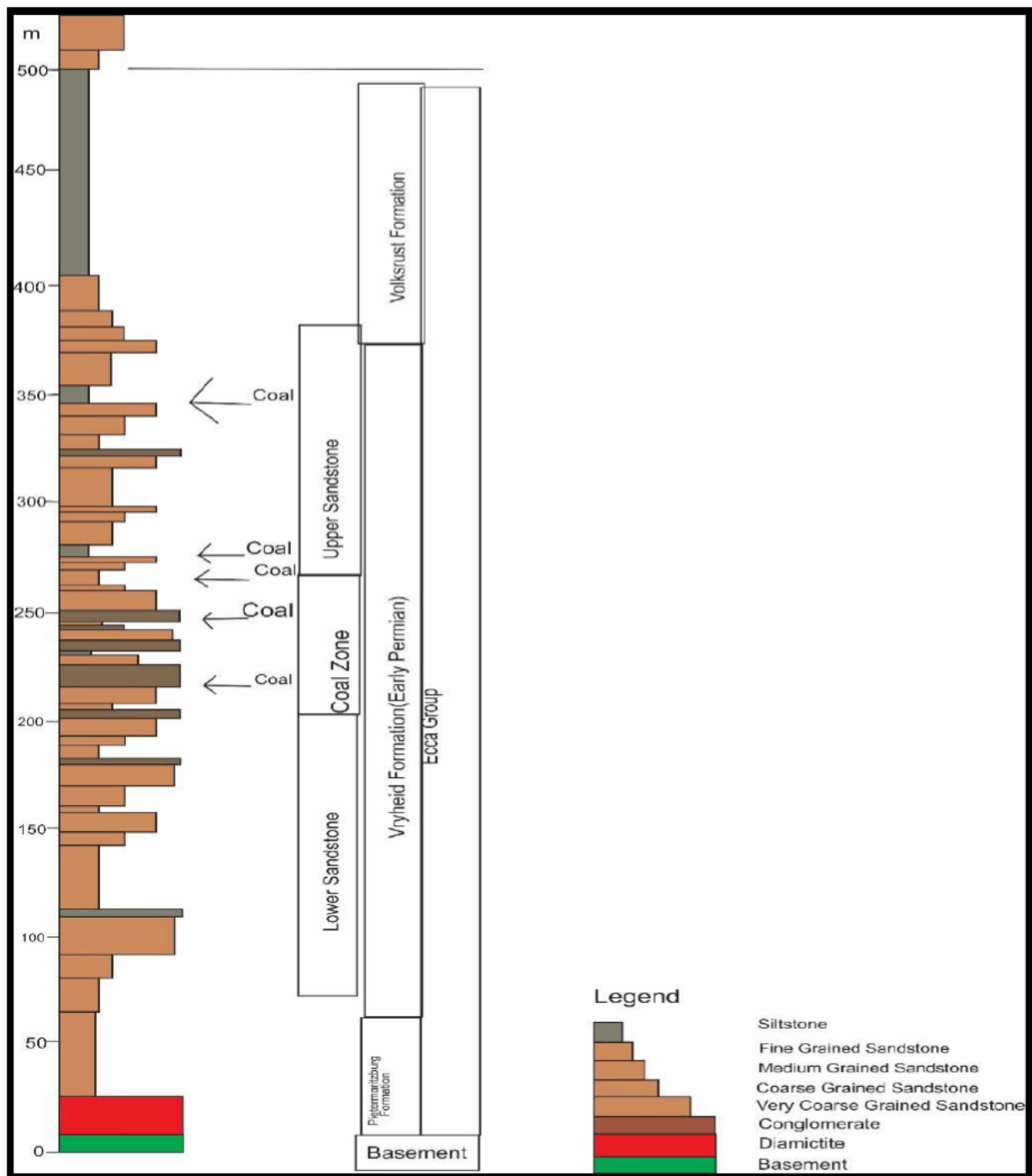


Figure 3.8. Stratigraphic subdivision of Klip River Coal fields, after Roberts 1988b in Hancox, and Götz, 2014.

3.2.6 Climate

The climate of KwaZulu-Natal is influenced by the Indian Ocean's warm Agulhas current successively creating a coastal region of subtropical climate (Fairbanks and Benn, 2000). This

climate is characterized by high temperatures, high humidity and high summer rainfall, experiencing warm wet summer and cool dry winter seasons (Fairbanks and Benn 2000). Figure 3.9 below indicates average rainfall patterns experienced in this province periodically from 1921 to 2019. Indicatively the province experienced the driest years receiving < 75% of rainfall and the wettest years receiving > 125% during this period (SAWA, 2020).

The Drakensburg escarpment forms a climatic boundary given its physiographic and altitudinal characteristics (Fairbanks *et al.*, 2001), resulting in the creation of orographic rainfall to the east and the highest mean annual precipitation of the country (Jewitt, 2018).

According to the new Köppen Greiger classification system to quantify climatic conditions, the Wasbank area, uMzinyathi District, KZN is designated as Cwb which is characterised as experiencing hot summers, dry winters and a warm temperate climate. Annual mean minimum temperatures range from 10.1°C and 16.7°C and 21.6°C and 23.9°C and annual mean maximum temperatures range from 24.2°C to 27.4°C to 40.1°C and 42.4°C respectively (SAWSA, 2020). Mean annual precipitation ranges from 550 millimetres (drier and low-lying regions) to 2000 millimetres with most rainfall occurring from October to January (Worlddata.info, 2021).

During the research period, the area experienced a warm and temperate climate, characterised by high summer rainfall exceeding that of the winter months. The mean annual temperatures recorded are 16.8 °C (Degree Celsius) /62.3 °F (Fahrenheit) (Table 3.1 below) (Climate-Data.org, 2019). The annual rainfall received was 616mm (2017), 597mm (2018), 616mm (2019) and 718mm (2020) (South African Weather Services Annual Report (SAWSA), 2018, 2019, and 2020).

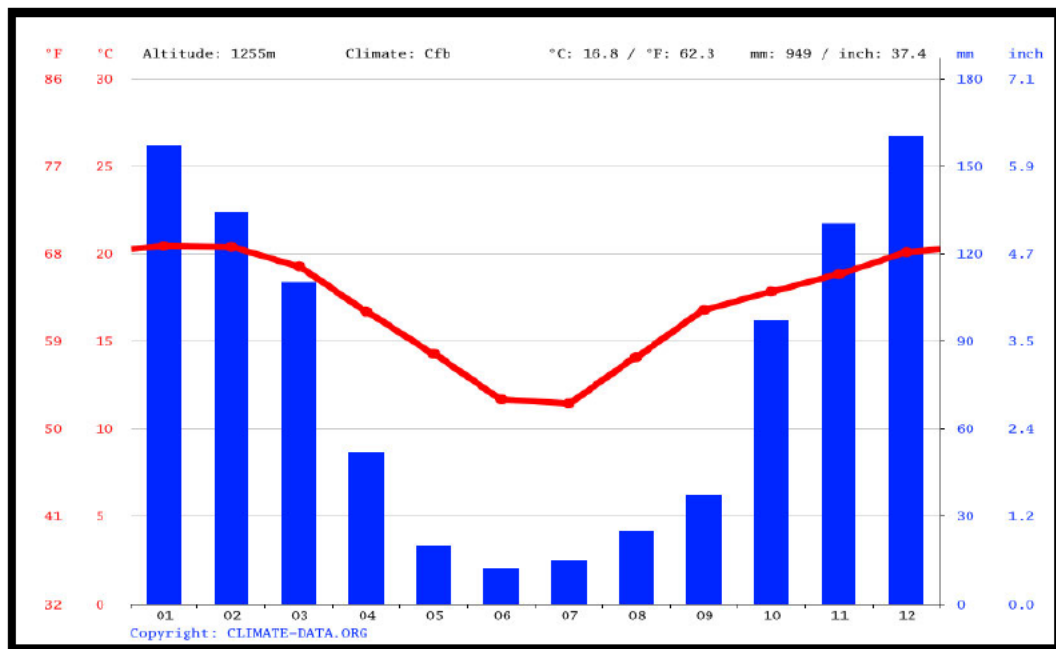


Figure 3.9. Annual climate graph for the study area (Climate-Data.org, n.d) (Adopted from SAWS, 2020).

During June and July, the average lowest mean temperatures and rainfall were recorded (Figure 3.9 above). The highest average rainfall was recorded in January, February, November and December, and the latter recorded the highest mean average monthly rainfall of 160mm (Table 3.1 below). The area falls within the Cwb Koppen and Geiger climate region. (South African Weather Service Annual Report (SAWSA, 2018; Climate-Data.org, n.d).

3.2.7 Vegetation

KwaZulu Natal contains five biomes and 101 vegetation types and subtypes, many of which are endemic (Jewitt, 2018), of which 52 vegetation types are threatened (Rushworth, 2015). The five biomes are: Savanna (3 259 341 ha), Grassland (4 583 855 ha), Indian Ocean Coastal Belt (891 092 ha), Wetlands (393 628 ha) and Forests (202 879 ha) (Jewitt, 2018).

Table 3.1. Mean Monthly weather averages for the study area (Climate-Data.org, 2019).

	January	February	March	April	May	June	July	August	September	October	November	December
Avg. Temperature °C (°F)	20.4 °C (68.8) °F	20.4 °C (68.7) °F	19.3 °C (66.7) °F	16.7 °C (62) °F	14.3 °C (57.7) °F	11.7 °C (53) °F	11.4 °C (52.6) °F	14.1 °C (57.4) °F	16.8 °C (62.2) °F	17.8 °C (64.1) °F	18.8 °C (65.9) °F	20.1 °C (68.1) °F
Min. Temperature °C (°F)	15.6 °C (60.1) °F	15.7 °C (60.3) °F	14.4 °C (58) °F	11.7 °C (53.1) °F	8.5 °C (47.4) °F	5.7 °C (42.3) °F	5.1 °C (41.2) °F	7.4 °C (45.4) °F	9.9 °C (49.7) °F	11.6 °C (53) °F	13.2 °C (55.7) °F	14.8 °C (58.7) °F
Max. Temperature °C (°F)	26.3 °C (79.3) °F	26.1 °C (79.1) °F	25.1 °C (77.2) °F	22.6 °C (72.7) °F	20.9 °C (69.6) °F	18.6 °C (65.5) °F	18.7 °C (65.6) °F	21.7 °C (71) °F	24.5 °C (76.2) °F	25.1 °C (77.1) °F	25.6 °C (78.1) °F	26.3 °C (79.4) °F
Precipitation / Rainfall mm (in)	157 (6)	134 (5)	110 (4)	52 (2)	20 (0)	12 (0)	15 (0)	25 (0)	37 (1)	97 (3)	130 (5)	160 (6)
Humidity(%)	71%	71%	69%	65%	55%	50%	47%	44%	46%	58%	64%	68%
Rainy days (d)	13	11	10	6	3	1	2	3	4	10	13	14
avg. Sun hours (hours)	7.6	7.9	7.6	7.5	8.2	8.1	8.3	8.5	8.4	7.9	7.9	8.2

Natural processes and anthropogenic activities in the province have influenced the current conservation status of vegetation in KZN. In 1990 the percentage of natural habitat was 65.8%, but this decreased to 57.7% in 2017. This habitat loss has been attributed to the change of use to the built environment, agriculture, timber plantations and dams (Ezemvelo KZN Wildlife, 2018/2019). Twenty vegetation types are critically endangered, 15 endangered, 17 are vulnerable and 49 are least threatened (Rushworth, 2015) as listed in Table 3.2 below.

Table 3.2 Summary of conservation status of KZN vegetation types of biomes adopted from Rushworth, (2015).

Biome	Critically Endangered	Endangered	Vulnerable	Least Threatened
Grassland	1	5	7	14
Savanna	2	1	4	12
Indian Ocean Coastal Belt	2	2	1	1
Forest	11	5	0	7
Wetland	4	2	5	15
Total	20	15	17	49

The vegetation type of the study area in Figure 3.10 below is classified as Thukela Thornveld, Income Sandy Grassland and Northern KwaZulu-Natal Moist Grassland. The dominant vegetation type is the Income Sandy Grassland which occupies much of the eastern half of the study area with some extensions to the west in the central part of the study area. On the other hand, the Thukela Thornveld borders the Income Sandy Grassland to the west and the Northern KwaZulu-Natal Moist Grassland borders the Income Sandy Grassland to the north and east. Seep wetlands are found variously within the study area, including the north, south, southeast, southwest, and central parts, but mainly in the southeast.

3.2.8. Bird, mammal, reptile, and other life.

This province contains eminent biodiversity levels and the Maputaland–Pondoland–Albany biodiversity hot spot (Nel *et al.*, 2015; Jewit, 2018). The representation of species groups in approximate numbers in this province is according to the following classes not following any particular taxonomic hierarchy: mammals (189 species); reptiles (167 species); birds (600 species); butterflies (595 species); plants (>5600 species); frogs (74 species); freshwater fish (86 species); and estuarine fish (107 species) (Rushworth, 2015) (Ezemvelo KZN Wildlife).

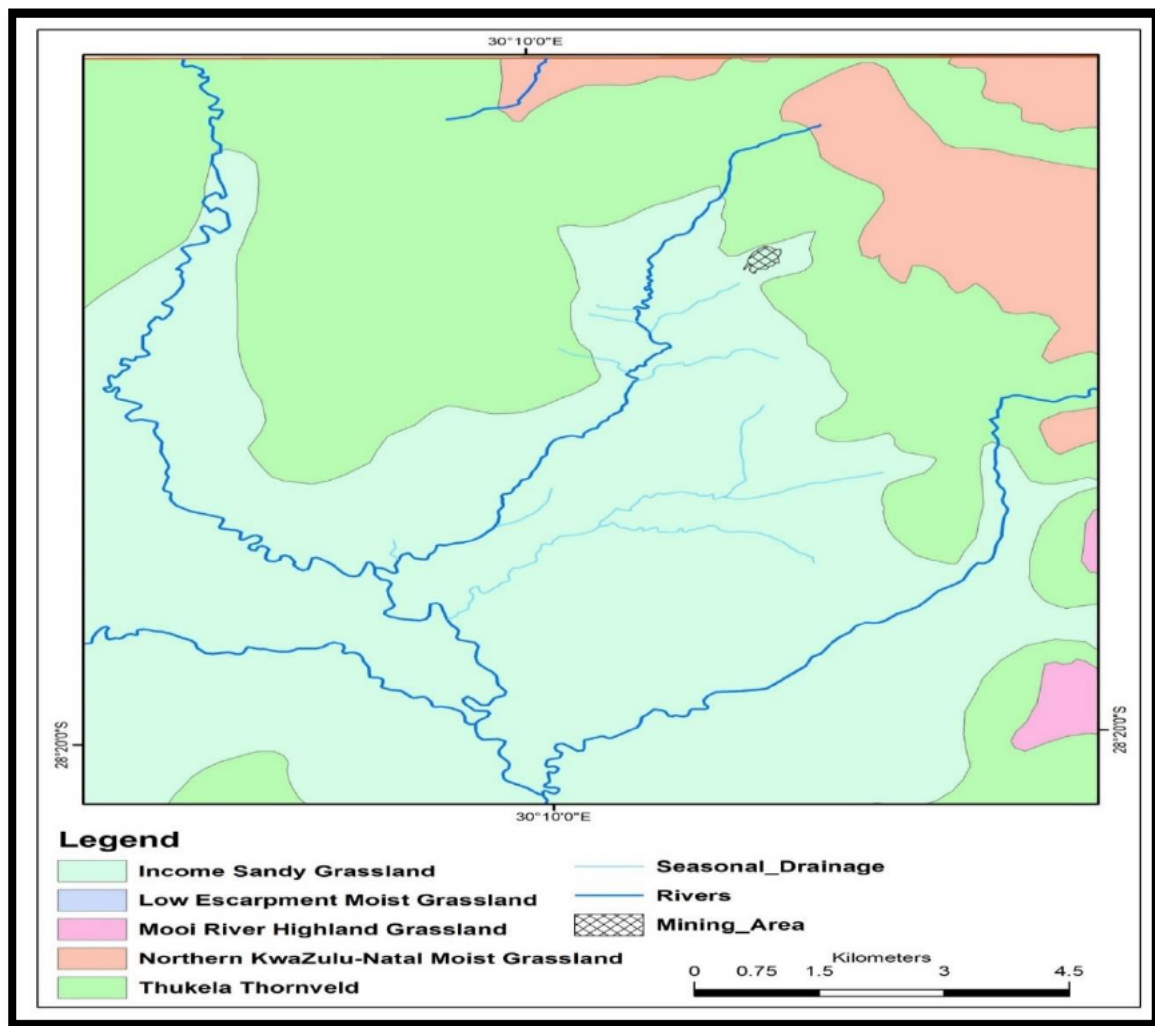


Figure 3.10. Vegetation and Wetland map of the study area.

3.4 Conclusion

The study area contributes significantly to the biodiversity, species richness and a wide range of landscapes and habitats. In addition, a comprehensive account of the topographical, drainage, climatic and geological characteristics associated with the study has been outlined. The environmental protection, conservation and preservation of this area are of paramount importance for the sustainability of the natural habitat and ecosystems; hence the consequences of AMD will be detrimental to the biodiversity and biota of the area. The methodology adopted for the study follows in the next chapter.

CHAPTER FOUR

RESEARCH METHODOLOGY

4.1 Introduction

This chapter presents a detailed account of the sampling procedures, laboratory analyses and statistical analyses adopted. In this study, an interdisciplinary approach was utilized with the aim of assessing the potential impacts of acid rock drainage or acid mine drainage in the Sandspuit Catchment, KwaZulu Natal.

The field sampling included coal discard samples from the mine dump and water resource samples from the two watercourses in the vicinity of the mine dump. Static and kinetic leachate testing was conducted in the laboratory and the procedures followed are presented in this chapter together with geochemical analyses used and, the waste rock classification of the coal discard. Water quality analyses were assessed chemically for samples collected in the field.

4.2 Research Methodology

The methodology implemented required the use of the following procedures to ascertain the impact of acid mine drainage/acid rock drainage:

- Field sampling of the Indumeni coal discard dump.
- Static testing (ABA-Acid Base Account and Net Acid Generation (NAG) Test) for classifying the samples as potentially acid-forming (PAF) or non-acid forming (NAF).
- Kinetic testing (leach column testing).
- Watercourse's sampling and chemical analysis of the water samples.
- Geochemical analysis (waste rock and leachates); and
- Waste rock classification (mineralogical assessment).

4.2.1 Desktop Study

A detailed desktop study was employed to determine background information on the research topic, geographic site, regional location, physiographic characteristics and an extensive literature review of the prediction and impacts of acid mine drainage and its implications for the water resources. This involved the use of aerial photography, Google Earth[®] and a literature survey that included journal articles, texts, internet articles, government legislation, policies,

and strategies. In this study, aerial photography was used to identify changes in the landscape as the target coal mine dump pre-dates 1965. Changes to the coal discard dump, landscape and surrounding area were studied using the images from Google Earth[®].

4.2.2. Field Surveys

A total of 33 site visits were conducted to the study area as part of this research. This included 5 site visits to the actual coal discard dump and 28 sampling visits for water sample collection. Sampling of the 2 watercourses was conducted monthly over a period of 28 months (November 2017 to February 2020), and sampling of the coal discard dump was conducted in November 2017 (Figure 3.5) at five sites (C1; C2; C3; C4; C5) on the Indumeni discard dump. The purpose of the above field surveys was to acquire knowledge on the acid mine drainage production at the coal discard mine dump; the quality of the discard leachate; the mineral composition of the discard, the water quality of the resources. This enabled assessment of the overall impact of the acid mine drainage from the discard mine dump into the surrounding water resources.

4.2.3 Primary Data Acquisition

Primary data was acquired as follows: sampling the 2 watercourses at five sites (sampling points R1; R2; R3; R4 and R5 as indicated in Figure 3.4), from November 2017 to February 2020. The first sample being in close proximity upstream to the coal discard dump and the rest of the samples downstream, below the dump. These samples were analysed for their physical, chemical, nutrient and heavy metal properties.

Five coal discard samples were collected once off from the coal discard dump (C1; C2; C3; C4; C5 as indicated in Figure 3.4). The following analyses/tests were carried out: total sulphur and carbon content; static testing; kinetic testing of coal discard; collecting and analysing the leachate from the test columns for the chemical, physical, nutrient, and heavy metal properties of the leachate samples (22 weeks); conducting ICP trace metal analysis, X-Ray fluorescence (XRF) for trace and major metal analysis and X-Ray diffraction.

4.2.3 Mine Discard Dump Sampling and Collection

As mentioned in the 'Study Area' chapter, the Indumeni coal discard dump was chosen for this study. Sampling on the mine discard dump was conducted as follows: The area was first assessed in terms of location, accessibility, and safety. Five sampling points were identified and mapped. The coal discard was collected using a Dutch soil auger and a spade. The coal

discard sample was placed into and sealed in plastic bags to prevent any further chemical reaction (oxidation) from taking place. At each sampling site, coal discard samples were taken at various depths due to the accessibility of material safety at the time of sampling as well as many saturated points on the dump. The coal was burning, (instantaneous combustion) (refer to Table 4.1 below). Samples were sealed in plastic bags which were then labelled together with a record of the GPS sampling position and thereafter transported to the laboratory. Each coal discard sample weighed approximately 2.5 kilograms.

Table 4.1. Coal Discard Sampling Points.

Sample Number	Depths of coal discard sample of dump	GPS-coordinates
1	0 to 30 cm	S28 14' 59.4'' E30 11' 52.7'' E
2	30 to 80 cm	S28 14' 57.3'' E30 11' 41.1'' E
3	1 meter	S28 15' 01.6'' E30 11' 40.9'' E
4	1.5 meter	S28 15' 01.6'' E 30 11' 44.7'' E
5	+25 meter	S28 15' 3.6'' E30 11' 35.2'' E

4.2.5 Water Quality Sampling

Five water quality sampling points (Refer to Figure 3.4 and Table 4.2) were identified as part of the monthly sampling monitoring program of the two watercourses (Biggarsgat and Wasbank River). The sampling points occur upstream of the coal discard dump, in the vicinity of the mined area and downstream of the discard dump. Water quality sampling was conducted for 28 sampling months, extending from 20 November 2017 (spring sample) to 18 February 2020 (summer sample). All water sampling was conducted with due care to ensure that no secondary contamination of the sample occurred during and after the sampling process. Sterile 500ml sample bottles were filled to maximum volume (100%) and securely sealed. All samples were labelled correctly indicating; GPS location, date and time and placed into cooler boxes with ice. The samples were transported to the Chemistry Laboratory of the University of KwaZulu-Natal for analysis.

Table 4.2. Description of the Watercourse Sampling Points (Refer to Figure 3.4).

Watercourse sample number	Name of sampling point	GPS coordinates
R1	Biggarsgatspruit River, upstream of the Indumeni Decant	S 28°14' 59.2" E -30°11' 52.8"
R2	Indumeni pop decant	S 28°17' 17.1" E -30°11' 30.0"
R3	Biggarsgatspruit River downstream lower Biggarsgat and Indumeni decant	S 28°16' 53.3" E -30°10' 14.7"
R4	Biggarsgatspruit River at De Kroon low-level bridge, upstream confluence of Wasbank River	S 28°17' 50.4" E -30°09' 36.7"
R5	Wasbank River downstream Biggarsgatspruit River on Wasbank-Dundee Road bridge	S 28°18' 36.4" E -30°08' 52.2"

4.3 Laboratory Analysis for Coal Mine Discard and Water Quality Samples

4.3.1 Coal Mine Discard Analysis

To calculate the potential of the discarded coal to neutralise or to generate acidity, the following, chemical analysis was conducted to ascertain the Acid-Base Account (ABA) and Net Acid Producing Potential (NAPP). Samples were subjected to the following tests: pH; EC; total sulphur and carbon determination. The results obtained from the above tests were used in determining the Maximum Potential Acidity (MPA), the Acid Neutralising Capacity (ANC), the net acid-producing potential (NAPP) and the ANC/MPA ratios. The samples were further subjected to the Single Addition Net Acid Generation (NAG), to oxidise any sulphide minerals in the sample as acid generation and acid neutralisation reactions can occur simultaneously (Smart *et al.*, 2002); and the Sequential NAG test, as the coal samples in this study contained high levels of sulphur content as well as to overcome incomplete oxidation in the NAG test.

The kinetic test procedure involved the use of humidity column tests for a period of 22 weeks and, geochemical characterisation of the coal discard for trace and major elements was determined using XRF and Laser Ablation ICP-MS.

The above is discussed in detail below.

4.3.1.1 Acid Base Accounting (ABA) (Static Testing) for Mine Discard Analysis

Acid-base accounting (ABA), is a type of static testing, is an analytical tool that was originally developed by scientists at West Virginia University in the 1960s and is used in the assessment overburden for the acid-producing potential and acid-neutralising potential prior to mining (Skousen *et al.*, 2002). This geochemical assessment has since been shown to be a reliable in determining the acid-producing and consuming potential of geologic material during exposure to the weathering process (Hageman *et al.*, 2015). ABA has thus become a widely adopted method to characterize overburdened material and to predict post-mining drainage quality (Sobek *et al.*, 2000 and Skousen *et al.*, 2001). The researcher employed this tool as part of the initial acid mine drainage investigative assessment on the coal discard dump.

The following methods hereon were adapted from Smart *et al.* (2002), “ARD test handbook: project P387A, prediction and kinetic control of acid mine drainage AMIRA, International Ltd, Ian Wark Research Institute, Melbourne, Australia (ABA-Static test) and the American Society of Testing Materials (ASTM) D5744-07, standard test method for weathering of solid materials using a humidity cell (Kinetic test)”.

The following investigative tests were conducted on the coal discard samples as part of the initial acid mine drainage assessment (ABA-static test): pH and electrical conductivity (EC); total sulphur and carbon analysis; acid neutralising (ANC) test; net acid-producing potential (NAPP); the single addition net acid generation (NAG) test and the sequential NAG test.

4.3.1.2 pH and Electrical Conductivity (EC) of the Coal Discard Slurry

The paste pH/EC analysis was determined by equilibrating the sample in deionised water for approximately 12 hours at a solid-to-water ratio of 1:2 (w/w) and measuring the pH and EC. This analysis indicated the salinity and acidity of waste material when initially exposed in the mine discard dump.

Procedure:

Twenty-five grams (25g) of pulverised (<75µm) discarded coal sample was placed into a beaker and distilled water (50 ml) was gradually added while stirring to form a slurry. The slurry was allowed to stand for 12 hours before the pH and EC measurements were taken (Smart *et al.*, 2002).

4.3.1.3 Total Sulphur and Carbon Analysis

The sulphur and carbon analyses were conducted using the Carbon Hydrogen Nitrogen Sulphur (CHNS), Elemental analyser.

Procedure:

A portion of the coal discard sample (dry and pulverized) was placed into a combustion chamber. The percentage of nitrogen, carbon, hydrogen and sulphur was obtained by means of the CHNS elemental analyzer. For this research, the percentages of carbon and sulphur were used.

4.3.1.4 Acid Neutralising Capacity (ANC) Test

Smart *et al.*, (2002) adapted the modified Sobek method (Sobek *et al.*, 1978) to determine acid neutralising capacity (ANC). This method was subsequently used to calculate the acid neutralising capacity (ANC) of the coal discard sample. Standardised hydrochloric acid (HCl) was added to 0.5 grams of finely ground coal sample allowing time to react (with heating). To determine the amount of unreacted HCl, the mixture was back titrated with standardised sodium hydroxide (NaOH) (Smart *et al.*, 2002).

Procedures:

There were 5 steps (A-E below) that were followed in determining the ANC of the coal discard samples. They are as follows:

- A)** In determining the concentration and amount of acid in the analysis, a 'fizz rating' was used on the pulverised coal samples, a mass of 0.5 g of the pulverised sample was placed on a ceramic plate and, adding one to two drops of 1:3 HCl (approximately 8% HCl) (Smart *et al.*, 2002). The bubbling or audible "fizz" (effervescence) indicated the presence of CaCO_3 . A rating was then given according to Table 4.3.1 below.

Table 4.3.1. Fizz Ratings and Associated Acid Quantities and Concentrations used in the ANC Determination.

Reaction	Fizz Rating	HCL Molarity(M)	HCL Vol (ml)	NaOH Molarity (M)
<i>No reaction</i>	0	0.5	4	0.1
<i>Slight reaction</i>	1	0.5	8	0.1
<i>Moderate reaction</i>	2	0.5	20	0.5
<i>Strong reaction</i>	3	0.5	40	0.5
<i>Very strong reaction</i>	4	1.0	40	0.5
	5*	1.0	60	0.5

*5 is used for material with very high ANC (> 400 kgH₂SO₄/t) e.g., limestone. Source: Adopted from Smart *et al.*, 2002).

- B)** A mass of 2.00 grams of pulverised, air-dried sample was placed in a dry, clean, 250 ml Erlenmeyer flask. The HCl (amount required as indicated in Table 4.3.1 above) was carefully pipetted into the beaker then adding approximately 20 ml of deionised water. Blank samples were also prepared (in duplicate) by pipetting the same concentration and volume of acid into clean beakers with no sample and adding 20 ml of deionised water. For each Fizz Rating used, blanks were run for each volume and/or concentration of acid (Smart *et al.*, 2002).
- C)** The beakers (covered with a watch glass) were heated (80 to 90°C) on a hotplate for 1 to 2 hours (or until the reaction completed), with occasional swirling of the beaker. The reaction was complete when the particles settled evenly, and no gas evolution was evident. Special precaution was taken to ensure the flasks did not evaporate to dryness (Smart *et al.*, 2002).
- D)** The beakers were cooled at room temperature, thereafter deionised water was added to give a total volume of ~125 ml. A pH measurement was then taken using a pH meter (Microprocessor pH meter). The pH values were in the region of 0.8 to 1.5, thereafter the researcher proceeded to step E. The pH values were greater than 1.5 for samples 3 and 4, (with a fizz rating of 2) and additional acid was required (except when the test was at a fizz rating of 0). In cases where the pH of the mixture was low (<0.8 except where the fizz rating was 5), the test was repeated as too much acid had been added.

E) Samples 3 and 4 were titrated against a sodium hydroxide (NaOH) standard solution constantly stirring (using NaOH molarity listed in Table 4.3.1 above). The titration was interrupted near pH 5 and 2 drops of 30% H₂O₂ were added for oxidation of any dissolved ferrous ion. The titration continued to pH 7.0 and the volume of NaOH added was recorded. The "blank" was titrated against NaOH shown in Table 4.1 below. and duplicates were run on every fifth sample.

Following the above, the ANC was then calculated using the following:

$$\text{ANC} = [\text{Y} \times \text{MHCl} / \text{wt}] \times \text{C} \dots\dots\dots \text{Equation (1)}$$

Where:

$$\text{Y} = (\text{Vol. of HCl added}) - (\text{Vol. of NaOH titrated} \times \text{B})$$

$$\text{B} = (\text{Vol. of HCl in blank}) / (\text{Vol. of NaOH titrated in blank})$$

MHCl = Molarity of HCl

wt = Sample weight in grams

C = Conversion factor

C = 49.0 (to calculate kg H₂SO₄/t)

C = 5.0 (to calculate % CaCO₃ equivalent)

Samples 1, 2 and 5 were within a fizz rating of zero and samples 3 and 4 were within a fizz rating of 2 (refer to Table 4.3.2 below) Samples with an ANC result falling in the specified fizz rating, indicated that a correct amount of acid had been added. Analyses were repeated for results that were outside of the lower and upper limits of the ANC at a different fizz rating.

Table 4.3.2. Upper and lower limits of ANC

Fizz rating	<i>0</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>
ANC lower limit	-	10	40	100	200	400
ANC upper limit	10	40	100	200	400	-

Source: Adopted from Smart *et al.*, 2002.

4.3.1.5 Net Acid Producing Potential (NAPP) calculation (based on Sulphur and ANC values)

The net acid-producing potential (NAPP) was used to determine the potential of the mine discard sample to generate acid mine drainage. This value of the NAPP represents a balance between the sample capacity to neutralise acid (ANC) capacity to generate acid (Maximum Potential Acidity-MPA) (Smart *et al.*, 2002). The NAPP is expressed in kg H₂SO₄/t.

Following the above, the NAPP was then calculated using the following:

$$\text{NAPP} = \text{MPA} - \text{ANC} \dots\dots\dots \text{Equation (2):}$$

If the MPA is less than the ANC then the NAPP is negative, which indicates that the sample may have sufficient ANC to prevent acid generation. If the MPA exceeds the ANC then the NAPP is positive, which indicates that the material may be acid-generating (Smart *et al.*, 2002). In this study, all samples yielded a positive NAPP value, indicating the net acid-producing potential of the samples.

4.3.1.6 ANC/MPA Ratio

An alternate way of assessing the acid-base account and risks of coal mine discard material is the ANC/MPA ratio (Smart *et al.*, 2002). The purpose of the ratio is to indicate the relative safety margin (or lack thereof) within material (Smart *et al.*, 2002). According to past research, safe values of ANC/MPA ratios were reported for the acid generation prevention. These values range from 1-3 (Table 4.3.3 below) (Smart *et al.*, 2002). A positive (+ve) NAPP is equivalent to an ANC/MPA ratio below 1 (<1), and a negative (-ve) NAPP is equivalent to an ANC/MPA ratio above 1 (>1) (Smart *et al.*, 2002). A NAPP of zero is equivalent to an ANC/MPA ratio equal to 1 (Smart *et al.*, 2002).

Table 1.3.3. NAPP Values versus ANC/MPA Ratio

NAPP	ANC/MPA Ratio
Positive (+ve)	<1
Negative (-ve)	>1
Zero (0)	1

Source: Adopted from Smart *et al.*, (2002).

All samples had an ANC/MPA ratio of less than 1, thereby confirming the acid generation risk from the Indumeni discard dump.

4.3.1.7 Single Addition Net Acid Generation (NAG) test

This test is used in with the calculated values derived from the net acid-producing potential of the sample (NAPP) (Smart *et al.*, 2002). Both acid generation and acid neutralisation reactions can occur simultaneously. The result is a net amount of acid generated by the sample and is expressed in kg H₂SO₄/t, known as the NAG capacity (Smart *et al.*, 2002). The NAG pH (pH range, 2 to 3.24) of all samples was acidic, thereby indicating a risk of acid generation. In this study, the standard procedure for conducting the NAG test was followed.

A mass of 2.5 grams of pulverised sample was placed into a conical beaker 500 ml. 250 ml of a solution of hydrogen peroxide was added (15% H₂O₂) (30% H₂O₂ diluted 1:1 with deionised water). A watch glass was used to cover the top of the beaker which was then placed in a fume hood. The sample reaction was completed at boiling and when effervescence stopped the sample cooled at room temperature. Deionised water was added for a total volume of 250 ml. The pH of the solution was then recorded as the NAGpH. The solution was titrated to pH 4.5 and 7.0 with NaOH. Following Smart *et al.* (2002), when the NAGpH was > 2 titration with 0.10 M NaOH was adopted and when NAGpH was = 2 titration with 0.50 M NaOH was adopted.

Following the above, the NAG was then calculated using:

$$\text{NAG} = (49 \times V \times M) / W \dots \dots \dots \text{Equation (3)}$$

Where:

NAG = Net acid generation H₂SO₄/tonne

V = Volume of NaOH used in titration (ml)

M = Concentration of NaOH used in titration (moles/litre)

W = Weight of sample reacted (g)

4.3.1.8 Sequential NAG Test

To overcome any limitations in the NAG test completed, a multistage sequential NAG test was further performed to prevent any incomplete oxidation that may have occurred due to a catalytic breakdown of hydrogen peroxide in the sample. This test obtains the maximum NAG

value in samples that have a NAG/MPA ratio of less than 5 (<5) Smart *et al.*, 2002). Samples 2-5 had a NAG/MPA ratio of <5.

The procedure followed is as follows:

A mass of 2.5 grams of pulverised sample was transferred into a conical flask (500ml). A volume of 250 ml of 15% H₂O₂ (30% H₂O₂ diluted 1:1 with deionised or distilled water) was added. The sample was placed in a fume hood and allowed to react for approximately 2 hours until effervescence ceased. After the reaction, the conical flask was placed on a hot plate (150 to 200°C) and heated until effervescence ceased. The Once the sample was cooled at room temperature, pH and EC readings were taken, then filtered. The NAG liquor was retained and used for the titration step. The solid residue was rinsed with deionised water to remove excess, unreacted H₂O₂. The sample was filtered, the liquor was discarded. The NAG liquor was titrated with continuous stirring to pH 4.5 and 7.0, with NaOH conc. based on the recommended NAGpH as follows (Smart *et al.*, 2002).

if NAGpH is > 2 Titrate with 0.10 M NaOH

if NAGpH is = 2 Titrate with 0.50 M NaOH

Following the above, the NAG was then calculated using the following:

Calculation of Net Acid Generation by:

$$\text{NAG} = (49 \times V \times M) / W \dots\dots\dots \text{Equation (4):}$$

Where:

NAG = net acid generation (kg H₂SO₄/tonne)

V = volume of NaOH used in titration (ml)

M = concentration of NaOH used in titration (moles/litre)

W = weight of sample reacted (g)

The NAG values for samples 1 and 5 exceeded 25 kg H₂SO₄ per tonne, and the procedure was repeated with a lower sample weight (1.0g). This completed the test procedures for the Acid-Base Account analysis (static testing). The results indicated all 5 samples as potentially acid-generating (PAF).

4.4 Kinetic Testing

Kinetic testing is a laboratory weathering procedure that involves various measurements over time to assess various acid mine drainage constituents (Smith *et. al.*, 2002; ASTM, 2007). These tests aid in the prediction of mine waste drainage quality (Sapsford *et al.*, 2009). The procedure is used to determine the acidic, alkaline, or neutral drainage of the sample; and identify solutes in the effluent; the mass of solutes released; and the rate at which solutes are released (ASTM, 2009). For this research focus was placed on the leachate chemistry of the coal discard leachate over a specific period to produce acidic, alkaline and or neutral drainage. The laboratory weathering of mine discard material was conducted using and operating humidity cells. This method was adopted by the American Society for Testing and Materials, (ASTM) International, issued under the fixed designation D5744-07. There are two protocols; Option A and Option B (refer to Table 4.4.1 below). Option B protocol was selected, and five (5) humidity cells were used in this research.

Each humidity cell is cylindrical and was constructed with material suited for this type of research (refer to Figure 4.0.). The cell wall thickness is 0.318cm and the height of the cylinder is 20.8cm. The cylinder was held by a base that is 1,27cm in thickness and the top is covered with a lid. Two polypropylene filter media, 22 um, 1 were inserted in the base of the cylinder prior to infilling of waste material and the other was placed on top of the waste material. The lid is then inserted to close the humidity cell. The centre of the lid has a hole that allowed for exchange of ambient air and for the infilling of deionised water for the weekly leach collection.

Table 4.4.1. Coal Discard Laboratory Weathering Procedures Test Protocols.

Laboratory Weathering Procedure Protocol Option A	Laboratory Weathering Procedure Protocol Option B
Each humidity cell stored undergoes, 3 days of dry air (<10% relative humidity) and 3 days of water-saturated air (approximately 95% relative humidity). This is pumped up into the sample, followed by a leach with deionised water on day 7.	Each humidity cell is stored for 6 days under conditions of controlled and relatively constant temperature and humidity. The oxygen (ambient air) is supplied to the sample by diffusion (and possibly advection) followed by a leach with deionised water on day 7.

Source: Adopted from ASTM, (2009).

Using the Humidity Cells, the following procedure, as recommended by the ASTM (2007), was followed:

- Coal discard materials collected per sampling site were crushed to pass through a 6.3mm (0.25) screen.
- 1000 grams of the crushed material was placed into each humidity cell and filled with one litre (1L) of deionised water to flush the leachate, i.e., a 1:1 ratio was applied.
- The humidity cells were stored for six days in the laboratory under conditions of relatively constant temperature, humidity, and oxygen by diffusion of ambient air, in an environmentally controlled enclosure; and
- Weekly leachates were collected and chemically analysed over a test duration of 23 weeks.



Figure 4.0. Humidity leach columns for the kinetic testing with weekly leachate.

4.5. Elemental Content of Waste Rock

4.5.1. X-Ray Fluorescence Spectrometry (XRF)

XRF was used to identify geochemical concentrations of trace and major elements for the coal discard. A PAN analytical Axios Wavelength Dispersive Spectrometer was used for the analysis.

An Rh tube was inserted into the spectrometer with the following analysing crystals: LIF220, LIF200, PE 002, Ge 111 and PX1. A scintillation detector and a gas-flow proportional counter was further fitted (CAF, 2021). Argon- 90% and 10% methane mixture of gas is used in the gas-flow proportional counter. Control standards used in the calibration procedure were in line with the range of concentrations of the samples (CAF, 2021). These standards were among NIM-G (Granite from the Council for Mineral Technology, South Africa) and BE-N (Basalt from the International Working Group) (CAF, 2021). The analyses were conducted by the Central Analytical Facilities (CAF), Stellenbosch University, South Africa. The procedure used by the CAF was as follows:

- Samples were crushed into a fine powder (particle size < 70 µm) with a jaw crusher and milled in a tungsten-carbide Zibb mill, thereafter, prepared to a fused disc for major and trace elements analysis.
- Cross-contamination of samples was avoided by cleaning the jaw crusher and mill with uncontaminated quartz between successive analyses.
- Glass disks were prepared for XRF analysis using 7 g of high-purity trace element and Rare Earth Element-free flux ($\text{LiBO}_2 = 32.83\%$, $\text{Li}_2\text{B}_4\text{O}_7 = 66.67\%$, $\text{LiI} = 0.50\%$) mixed with 0.7g of the powder sample, and
- Mixture of sample and flux were fused in platinum crucibles with Claisse M4 gas fluxer at temperatures between 1100°C -1200°C.
- Major elements were analysed using a 2.4kW Rhodium tube. Matrix effects in the samples were corrected by applying theoretical alpha factors and measured line overlap factors to the raw intensities measured with the Super Q PAN analytical software.

4.5.2 Laser Ablation ICP-MS

To identify trace elements Inductively coupled plasma–mass spectroscopy (ICP-MS) was used for the coal discard samples.



Figure 4.1. The PAN analytical Axios Wavelength Dispersive spectrometer used for whole rock element composition determination (CAF, 2021).

The procedure used by the CAF follows the guidelines from Eggins, (2003). The procedure is as follows:

- Prior to analysis the ICP-MS was optimized for low oxide ratios and sensitivity (< 0.2%) by tuning both the ICP and laser parameters while ablating a line on NIST612.
- Just before introduction into the ICP plasma the ablation was performed in helium gas at a flow rate of 0.35L/min and then mixed with argon (0.9L/min) and nitrogen

(0.003L/min). For traces in fusions, 2 spots of 104 μ m are ablated on each sample using a frequency of 8Hz and fluence of ~ 3.5 J/cm².

- Fusion disks were prepared by an automatic Claisse M4 Gas Fusion instrument and ultrapure Claisse Flux, using a ratio of 1:10. Samples were coarsely crushed, and a chip of sample mounted in a 2.4cm round resin disk. The mount was mapped and then polished for analysis.
- NIST 610 glass (values from Jochum *et al.*, 2011) was used for quantification and analysis along with BCR-2G & BHVO-2G (values from GeoReM: Jochum *et al.*, 2005).
- To verify the effective ablation of fused material, a fusion control standard from certified basaltic reference material (BCR-2, and BHVO-1, (values from Jochum *et al.*, 2016) was analysed in the beginning of a sequence.
- LA-ICP-MS data reduction software package was used for processing the data.
- An internal standard element of known concentration was used to correct variations in ablation yield between samples and standards (Longerich *et al.*, 1996; CAF, 2021). XRF analysis determined Al₂O₃ content of each sample.



Figure 4.2. A Resolution 193nm Excimer laser from Applied Spectra connected to an Agilent 7700 Q ICP-MS (CAF, 2021).

4.5.3 Mineralogy of Waste Rock: X-Ray Diffraction

XRD identified major phases in the sample. This was then matched against diffraction peaks to confirm the various major phases. A D8 Advance diffractometer was used in the analysis for powder coal samples. were acquired using a D8 Advance Figure 4.4. Samples were analysed in accordance with standard best practice using open polystyrene a sample holder shown in Figure 4.3. Measurements were performed against parameters summarised in Table 4.5. XRD was used to identify major phases in the sample. This was then matched against diffraction peaks to confirm the various major phases. A D8 Advance diffractometer was used in the analysis.

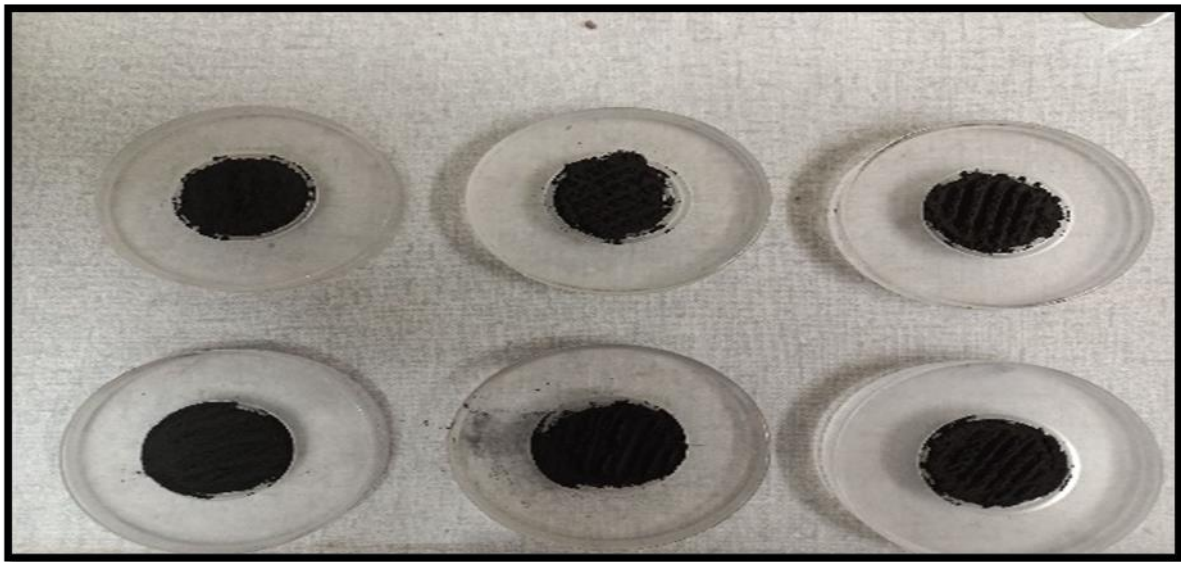


Figure 4.3. Coal samples analysed for phase identification.

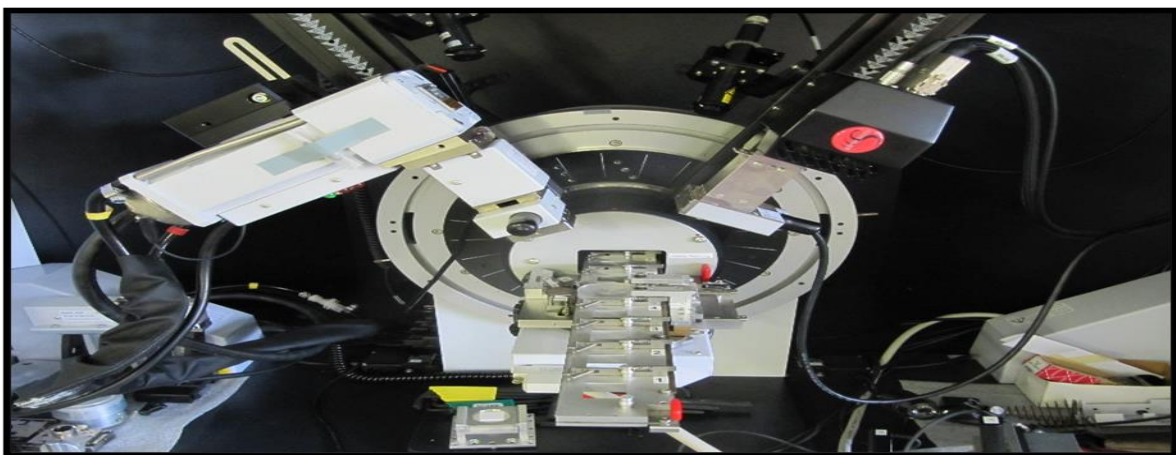


Figure 4.4. D8 Advance diffractometer indicating the flip stick sample stage (front centre of photograph) used for the analysis.

The Search/Match technique was used for the qualitative identification of the crystallographic phases. The International Centre for Diffraction Data (ICDD) PDF-4+ 2021 database was used to measure the diffraction peaks using the Sieve+ software. No data smoothing was performed. Quantification and crystallinity determination of the proposed phases were carried out using the Rietveld refinement method (TOPAS v6 software). This was performed by the South African Nuclear Energy Corporation (NECSA).

4.6. River Water Quality and Leachate Analysis

Water quality analysis for both the coal discard samples (leachate collected) and river water samples formed an integral part of understanding the chemical composition of the leachate and the hydrochemistry of the watercourses to determine the impact of AMD in the study area. The samples (both coal discard leachate and river water samples collected) were analysed to determine their physiochemical, nutrient, and heavy metal characteristics. All parameters analysed were identical for both the leachate and river water samples. The results emanating from the analyses were compared to the South African Water Guidelines Target Water Quality Ranges (TWQR) from the Department of Water and Sanitation for domestic, industrial, and aquatic ecosystems. The analysis was conducted at the University of KwaZulu-Natal chemistry laboratory.

4.6.1. Leachate and River water

The leachate and river water samples collected for analysis followed the same methodology and instrument used for analysis (refer to Table 4.5 below for the comprehensive list of parameters and methods of analysis). The discussion below relates to both the leachate and river water samples. All samples were analysed in triplicate.

Table 4.5. Comprehensive table of parameters tested and method of analysis.

Parameter	Chemical Symbol	Unit of Concentration	Unit Symbol	Standard Method
Aluminium	Al	Milligrams per litre	mg/L	Inductively-Coupled Plasma Optical Emission Spectrometry
Cadmium	Cd	Milligrams per litre	mg/L	Inductively-Coupled Plasma Optical Emission Spectrometry
Calcium	Ca	Milligrams per litre	mg/L	Inductively-Coupled Plasma Optical Emission Spectrometry
Cobalt	Co	Milligrams per litre	mg/L	Inductively-Coupled Plasma Optical Emission Spectrometry
Copper	Cu	Milligrams per litre	mg/L	Inductively-Coupled Plasma Optical Emission Spectrometry
Chloride	Cl	Milligrams per litre	mg/L	Photometric - colourimetric
Chromium	Cr	Milligrams per litre	mg/L	Inductively-Coupled Plasma Optical Emission Spectrometry
Electrical conductivity	EC	Millisiemens per meter	mS/m	Photometric - electrochemical
Iron	Fe	Milligrams per litre	mg/L	Inductively-Coupled Plasma Optical Emission Spectrometry
Lead	Pb	Milligrams per litre	mg/L	Inductively-Coupled Plasma Optical Emission Spectrometry
Magnesium	Mg	Milligrams per litre	mg/L	
Mercury	Hg	Milligrams per litre	mg/L	Inductively-Coupled Plasma Optical Emission Spectrometry
Nickel	Ni	Milligrams per litre	mg/L	Inductively-Coupled Plasma Optical Emission Spectrometry
pH	pH	N/A	N/A	Photometric - electrochemical
Potassium	K	Milligrams per litre	mg/L	Flame Emission Spectroscopy
Sodium	Na	Milligrams per litre	mg/L	Flame Emission Spectroscopy
Total dissolved solids	TDS	Milligrams per litre	mg/L	Gravimetric analysis
Sulphate	SO ₄	Milligrams per litre	mg/L	Ion-Selective Electrode (ISE)
Zinc	Zn	Milligrams per litre	mg/L	Inductively-Coupled Plasma Optical Emission Spectrometry

4.6.1.1 Physio-chemical analysis.

The pH measurements were carried out using the Microprocessor pH meter and electrical conductivity (EC) was measured using the *Inolab Con Level 1 Multiparameter Meter*. Both parameters were measured in triplicate.



Figure 4.5. The Microprocessor pH meter (right) and the Inolab Con Level 1 Multiparameter Meter (left) were used in the measurements.

4.6.1.1. Nutrient Sampling (Sulphate).

The sulphate analysis was conducted using an ion-selective electrode (ISE) (Hanna solid state combination ion selective electrode). Leachate and river water samples were filtered by use of a 0.45-micron filter into 1.5 ml ICP vials. The sulphate concentration was quantified using Hanna's solid-state combination sulphate ion selective electrode (Hanna Instruments®). This electrode consists of a potentiometric cell housing a silver/silver chloride (Ag/AgCl) reference electrode immersed in a potassium nitrate electrolyte system. A compressed lead sulphide sensing membrane are isolated from the sample and the internal elements.

4.6.1.2. Heavy Metal Analysis

Heavy metal analysis was conducted using a *Perkin Elmer 8300 DV Inductively Coupled Plasma Optical Emission Spectrometry* (ICP-OES). This spectroscopic technique is based on

emission of photons from atoms and ions that have been excited in a radiofrequency (RF) discharge (Helaluddin *et al.*, 2016). This highly sensitive technique has immense advantages in the determination of heavy metals as outlined by Chand and Prasad (2013).

Leachate and river water samples were filtered with a 0.45-micron filter into 15 ml ICP vials. The samples were acidified with nitric acid (HNO₃). Heavy metals were analysed in triplicate including: Calcium (Ca); Aluminium (Al); Cadmium (Cd); Cobalt (Co); Copper (Cu); Chromium (Cr); Iron (Fe); Mercury (Hg); Nickel (Ni); Zinc (Zn) and Lead (Pb). A range of multi element standards was used to prepare calibration data for sample heavy metal (refer to Table 4.5) quantification. The analyses were performed in triplicate, and averages were taken as the final analysed result.



Figure 4.6. Perkin Elmer 8300 DV Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for leachate and river water analysis.

4.6.1.3. Sodium and Potassium Analysis

Flame Photometry was used to determine the concentration of Potassium and Sodium from the leachate and river water samples collected (Figure 4.7 below). Samples for Sodium and Potassium were filtered with 0.45 micro filter into 15ml ICP vials. The samples were un-acidified. The analysis was concluded using the Flame Photometer.



Figure 4.7. Flame photometer was used for sodium and potassium analysis of leachate and river water analysis.

4.7 Statistical analysis

The extensive data collected in this research was tabulated into spreadsheets using Microsoft Excel® 2010 and summary statistics were determined. Mean values for all results in triplicate were determined as were the measures of standard deviation and standard errors.

IBM SPSS Statistical software version 27 was used to perform multivariate statistical methods (MANOVA) as well as non-parametric rank-sum tests were employed including Spearman's correlation, Kruskal-Wallis test and a post-hoc Mann-Whitney U test. The Kruskal-Wallis test followed by a Mann-Whitney test was conducted using a Bonferroni correction of $\alpha=0.005$ was performed to determine if parameters differ significantly based on the location of sites and, relative to the coal discard dump (Helsel and Hirsch, 1992). This was adopted for the water quality and kinetic leach results.

In addition, the water quality index (WQI) of the river data were calculated based on the TWQR of DWS and compared to the WQI ranges established by Brown *et al.*, 1972.

Table 4.6. Status categories of the WQI (Brown, *et al.* 1972)

WQI	STATUS OF THE WATER
0 - 25	Excellent
26 - 50	Good
51 - 75	Poor
76 - 100	Very poor
>100	Unfit for domestic use

4.8 Conclusion

This chapter provided an in-depth account of the various methods adopted for the study. The detailed acid-base accounting procedures in the static test, kinetic leach column testing, XRF and XRD analyses formed part of the acid mine prediction procedures to determine the acid-generating potential. The water quality analysis and WQI determined the compliance levels of the river system and categorisation in terms of fitness for use. The procedures are in line with international best practice adhering to stringent quality control. The results emanating from the adoption of the above methodology are presented in the form of scientific papers in the next chapter.

CHAPTER FIVE

RESULTS

5.1 Introduction

This section presents the results from various comprehensive assessments conducted to forecast the prediction of acid mine drainage from an abandoned coal discard dump and its impacts on the Biggarsgatspruit and Wasbank Rivers. The integrated investigative research encompassed static testing (acid-base accounting-ABA), kinetic leach column testing, geochemical, mineralogical analysis of the coal discard and water quality analysis.

Reference is made to the following the results of the static testing (acid-base accounting) indicated initial acid-generating capacity of the abandoned discarded coal dump, whereas the kinetic leachate column testing was used to assess the geochemical quality of leachate. The physiochemical and heavy metal parameters of the leachate were compared to the Department of Water and Sanitation (DWS) Target Water Quality Range (TWQR). Furthermore, the coal discard was analysed for ICP trace metal analysis, and X-ray fluorescence (XRF) for major and trace metal analysis and mineralogical analysis was conducted using X-ray diffraction technique (XRD), for mineral phase identification.

The study's final assessment involved sampling of the two water resources, Biggargatspruit and Wasbank River over a test duration of 28 months. The sampling included upstream, and below the coal discard dump and downstream sample points. The results were compared to DWS (TWQR) for Aquatic Use. In cases where the TWQR for the aquatic use was unavailable, the domestic use water quality guideline was used as an alternative. The Water Quality Index (WQI) was performed to determine the fitness of use according to the status categories of the river system according to WQI (Brown *et al.*, 1972). In addition, to determine the inferences in the study from the results obtained, statistical analyses were performed on the results.

5.2 Presentation of the results

The study results are presented in three research papers, each focused on the main themes mentioned above: Static Testing, Kinetic Testing and Water Quality Assessment. The papers are presented below as per submission to the journals.

Paper 1: An Assessment of the impacts of the Indumeni coal discard dump on the Water Quality of Biggarsgatspruit and Wasbank Rivers, KwaZulu-Natal, South Africa.

Journal Submitted to: Water Resources Management.

Paper 2: The Characterization of Acid Mine Drainage using Static Testing at the Abandoned Indumeni Discard Dump Site, uThukela Water Management Area, KwaZulu-Natal, South Africa.

Submitted to Environmental Geochemistry and Health.

Paper 3: Kinetic Testing of Acid Mine Drainage from the Indumeni Discard Dump Site, Klip River Coalfields, KwaZulu-Natal, South Africa.

Submitted to Environmental Earth Sciences.

Paper One

An Assessment of the impacts of the Indumeni coal discard dump on the Water Quality of Biggarsgatspruit and Wasbank Rivers, KwaZulu-Natal, South Africa.

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Abstract

Water is vital for life on Earth, but this resource rapidly degraded, making it increasingly scarce. The rate and extent of water contamination have increased in concord with human population growth and natural resource exploitation. In South Africa, coal mining has contributed significantly to the economy but also led to considerable despoilation of surface water resources. In the KwaZulu-Natal province (KZN), numerous abandoned coal mines and discarded dumps have led to long-term environmental degradation. In this study, the impacts of the Indumeni discard dump site (IDDS), located near Wasbank in northern KZN, is investigated. Water from five river sites along the Biggarsgatspruit River sampled over 28-months were analyzed for a range of physicochemical parameters. Results indicate that the river system water quality was not fit for use as eleven of seventeen parameters exceeded the South African standards (Al, TDS, Cr, Cu, Na, Hg, EC, Zn, Pb, Cl and Cd). Statistical analyses using the Spearman's correlation, the Kruskal-Wallis test and the Mann-Whitney U test confirmed significant contamination of several parameters, as well as the variability of contamination status between sites and a series of parameter associations between site pairs. Assessment of the water quality using the water quality index (WQI) revealed very poor composite quality of the surface water sampled at all five sites, with Site 2, located just downstream of the discard dump categorised as unfit for domestic use. The results suggest that the IDDS is not solely responsible for the contamination, it is a major contributor. It is therefore recommended that comprehensive mine water management control be implemented in this catchment area for water resource protection for the aquatic biota, livestock, agricultural and domestic use.

Introduction

Water is critical for all life on earth, from micro-organisms to humans, (Kamble and Kumbhar, 2019) and at present this valuable natural resource is becoming progressively scarce and degraded as increasing amounts of water are required for a rapidly growing world population (Mishra *et al.*, 2021). Climate change has further exacerbated the global water crisis (Mishra *et al.*, 2021), due to both natural and anthropogenic causes (Mujere and Moyce, 2018).

Water resource management is currently of paramount importance across all water use sectors. Water quality depends on the chemical, physical and biological parameters that determine the fitness of use across the various water use sectors (mining, industrial, local government, and agriculture) to ensure economic growth and sustainability.

With respect to the mining industry, coal has been a major global resource (Welch, *et al.*, 2021; Acharya and Kharel., 2020) contributing strategically to ensure significant enhancement of economic growth (Welch *et al.*, 2021; Masood *et al.*, 2020; Acharya and Kharel, 2020). However, the coal extraction process is generally conducted under complex hydrogeological environments creating a plethora of water quality problems in the environment (Kamble and Kumbhar, 2019). This eventually leads to lower water tables, disrupts natural drainage patterns, leading to surface and sub-surface contamination, impacting water quality severely (Masood *et al.*, 2020).

For coal mining, considerable amounts of discarded material have been stored in dumps of diverse sizes and have caused pollution of water resources (Welch *et al.*, 2021). Mining waste containing sulphide minerals has the potential to cause acid mine drainage (AMD) when in contact with oxygen and water (Olías *et al.*, 2020). This phenomenon of AMD occurs in both abandoned and active mines (Tomiya and Igarashi, 2022). The oxidation process releases acidity, sulphates, and toxic levels of metals into the surrounding water resources (Olías *et al.*, 2020), subsequently leading to acidic drainage. The occurrence is contingent upon the composition and proportions of carbonate and sulphide minerals, as well as the dissolution kinetics of such minerals (Olías, *et al.*, 2020), leading to environmental hazards that pose a serious threat to river ecosystems worldwide (Ushakova *et al.*, 2022). This environmental issue is impacting numerous locations globally (Olías *et al.*, 2020).

In South Africa, mining is a primary activity that drives the economy, and coal mining is one of the key mining activities apart from gold mining. The main coal mining areas are in the provinces of Mpumalanga and KwaZulu-Natal and both areas have suffered significant environmental degradation/deterioration due to surface and sub-surface contamination from toxic pollutants.

This paper focuses on the impacts experienced by the surrounding water resources from an abandoned coal mine dump located in the Klip River Coal Fields of KwaZulu-Natal.

Study Site

The study area is located at GPS coordinate 28°14'57.29" S 30°11'40.76" E, near the town of Wasbank within the uMzinyathi District and the Endumeni Local Municipality (Figure 1). The

Klip River Coal field is the largest in northern KwaZulu-Natal. Other towns adjacent to the study area include Dundee and Glencoe. The Indumeni Discard Dump Site (IDDS) is situated within the Sandspruit Catchment (a secondary catchment to the larger uThukela Catchment) and the Biggarsgatspruit and the Wasbank Rivers (Figures 1 and 2) are the two tributaries that flow in close proximity to the dump site. Hence the water quality assessment of these two tributaries formed the focus of the study. This region experiences a temperate, warm climate, characterised by high summer rainfall and relatively drier winter months with an annual mean of 616mm (South African Weather Service Annual Report. 2018, 2019, and 2020). The mean annual temperature is 16.8 °C, however, summers are warm (23 to 27°C), and winters are cold (3 to 19°C) (Climate-Data.org, 2019).

Geology of the study site

The geology of the study site is part of the Vryheid formation (Ecca Group), occurring between the Late Carboniferous Dwyka Group and the Late Permian-Middle Triassic Beaufort Group (Catuneanu *et al.*, 2005). The sedimentary rocks that form part of Vryheid Formation represents some of the most distal facies of the Ecca interior seaway (Green *et al.*, 2012). This was deposited during gradual transformation from marine to non-marine conditions leading to the formation of extensive coal deposits within a mudstone–sandstone succession (Green *et al.*, 2012). This coal formation is categorized as bituminous and anthracite coal and characterised by elevated concentration of phosphorous and sulphur (Jeffery *et al.*, 2015).

Land use cover of the study site

The study area is classified as Thukela Thornveld, Income Sandy Grassland and Northern KwaZulu-Natal Moist Grassland. The dominant vegetation type is the Income Sandy Grassland which occupies much of the eastern half of the study area with some extensions to the west in the central part of the study area. Commercial agriculture, plantation and sugar cane farming are the main activities within this district (UMDM, 2019) however the study area includes an abandoned mine and is dominated by livestock farming.

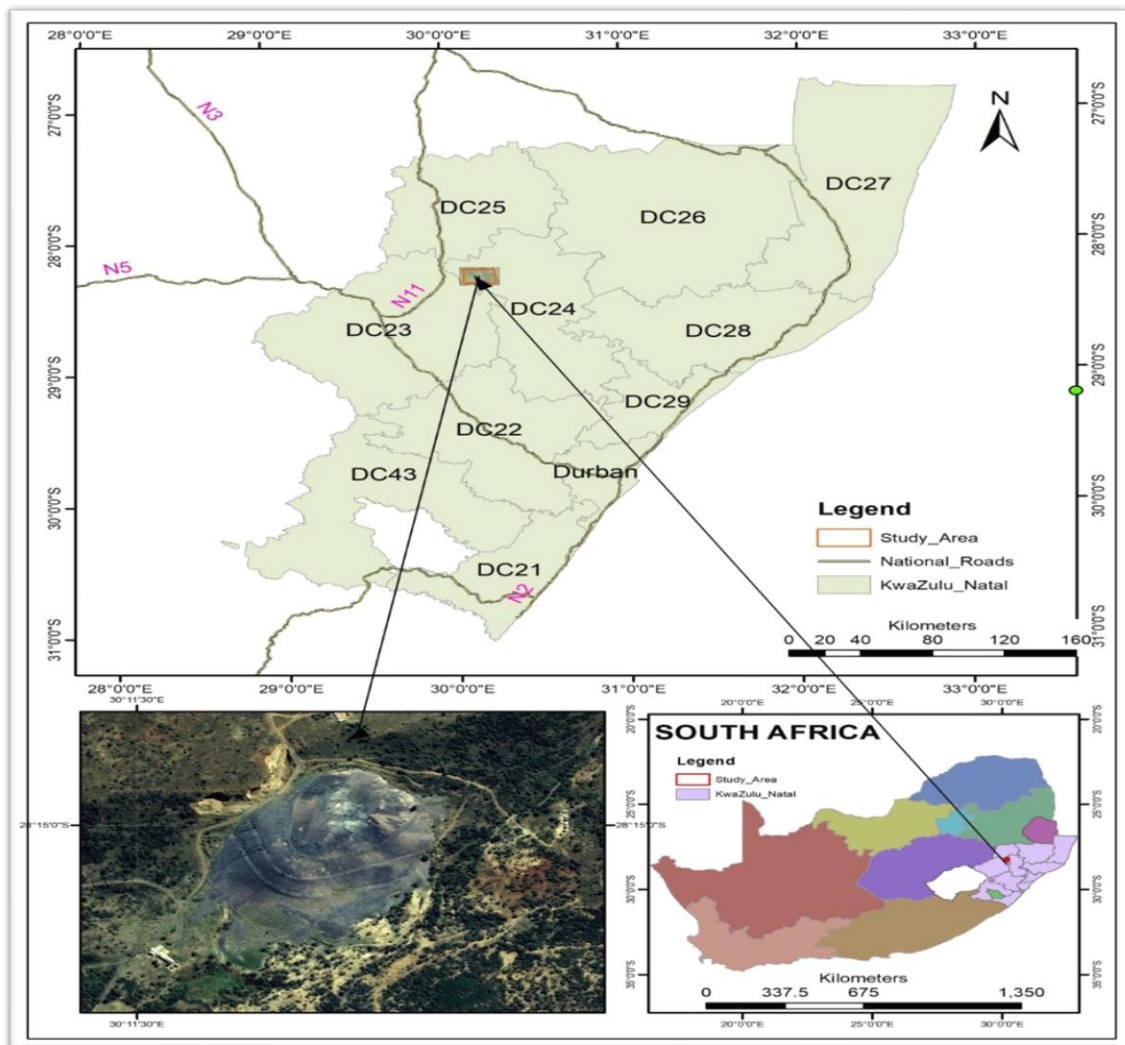


Figure 1: Location of the study area within uMzinyathi District in KZN, South Africa. The Indumeni discard dumpsite (IDDS) is shown on the bottom left. (Adopted from Govender S, 2025 submitted for publication).

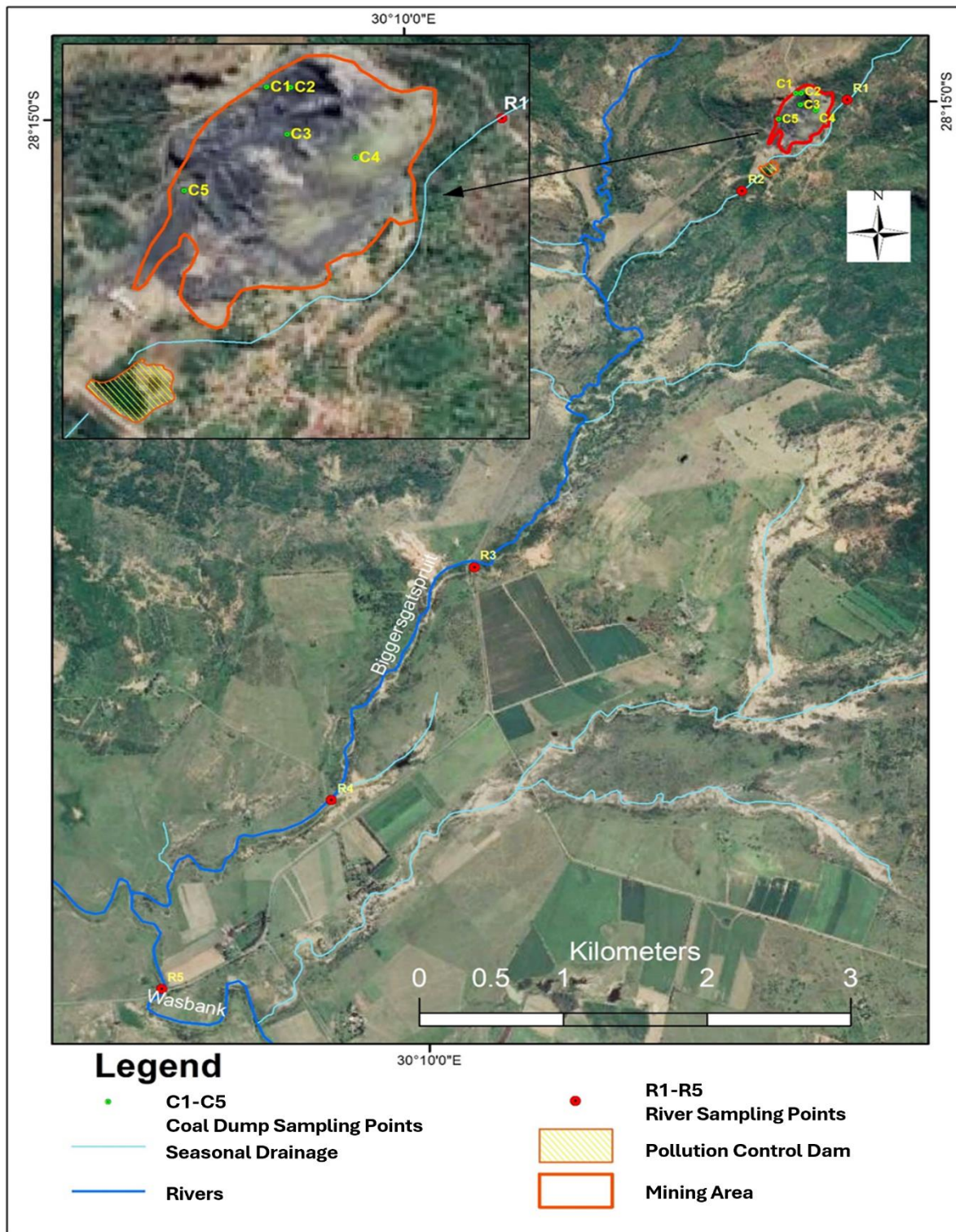


Figure 2: The study area indicating the five water resource sampling sites (R1 to R5) on the Biggarsgspruit and Wasbank Rivers.

Methods

Water quality sampling

Five water sampling sites (R1 to R5), as shown in Figure 2. and Table 1, were established as part of the monthly water sampling program of the two watercourses (Biggarsgatspruit and Wasbank Rivers) for the duration of the sampling programme. The sampling sites were located both upstream and downstream of IDDS. Sub surface grab sampling at a depth of 0-20cm in the midpoint of the river system was conducted over twenty-eight (28) months, extending from 20 November 2017 (spring sample) to 18 February 2020 (summer sample). The marked dichotomy in summer-to-winter rainfall in the region resulted in the river systems drying up during winter, resulting in numerous no-flow sampling days.

Table 1: Geographic Location of Sampling Sites.

Sample number	Name of sampling point	GPS coordinates
R1	Biggarsgatspruit River, upstream of the Indumeni Decant	S 28°14' 59.2" E -30°11' 52.8"
R2	Indumeni pop decant	S 28°17' 17.1" E -30°11' 30.0"
R3	Biggarsgatspruit River downstream lower Biggarsgatspruit and Indumeni decant	S 28°16' 53.3" E -30°10' 14.7"
R4	Biggarsgatspruit River at De Kroon low-level bridge, upstream confluence of Wasbank River	S 28°17' 50.4" E -30°09' 36.7"
R5	Wasbank River downstream Biggarsgatspruit River on Wasbank-Dundee Road bridge	S 28°18' 36.4" E -30°08' 52.2"

Consequently, no-flow sampling days yielded no samples. All water sampling was conducted with due care to ensure that no secondary contamination of samples occurred during and after the sampling process. Sterile 500ml sample bottles were filled to maximum volume (100%) and securely sealed. All samples were labelled indicating GPS location, date and time and transported on ice to the chemistry laboratory at the University of KwaZulu-Natal for analysis.

The water quality results thus obtained were compared to the South African Water Quality Standards known as the Target Water Quality Ranges (TWQR) and serves as a management tool formulated by the Department of Water Affairs and Forestry (DWAF), currently known as the Department of Water and Sanitation (DWS). The TWQR is designed to ensure no detrimental effects on the health of the aquatic ecosystem ensuring the protection of the water resources in South Africa (DWAF, 1996a; 1996b; 1996c; 1996d).

Laboratory Methods

Physiochemical parameters of the water samples were analysed; and elemental constituents (anions, cations, trace elements and heavy metals). The parameters analyzed were pH; total dissolved solids (TDS); electrical conductivity (EC); potassium (K); sodium (Na); calcium (Ca) sulphate (SO₄) and chloride (Cl). The pH was measured using the standard laboratory Microprocessor pH meter and electrical conductivity (EC) was measured using the *Inolab Con Level 1 Multiparameter Meter*. TDS was calculated as: $\text{TDS (mg/l)} = \text{EC (mS/m at 25 EC)} \times 6.5$ (DWAF, 1996c) and expressed in mg/l. Chlorides were analysed using the colorimetric method, sulphates were analysed using the Ion-Selective Electrode (ISE). Potassium, calcium, and sodium were analysed using flame photometry. Heavy metal analysis was conducted using a *Perkin Elmer 8300 DV Inductively Coupled Plasma Optical Emission Spectrometry* (ICP-OES). This spectroscopic technique is based on the emission of photons from atoms and ions that have been excited in a radiofrequency (RF) discharge (Helaluddin *et al.*, 2016). The following heavy metals were analysed: Calcium (Ca); Cadmium (Cd); Aluminium (Al); Cobalt (Co); Chromium (Cr); Iron (Fe); Copper (Cu); Mercury (Hg); Nickel (Ni); Zinc (Zn) and Lead (Pb). A range of multi element standards was used to prepare calibration data for sample heavy metal quantification. The analyses were performed in triplicate and the average analysed.

Statistical Analysis

The data collected in this project was collated and statistically analysed using IBM SPSS Statistics V27. To evaluate and characterise water quality data and to facilitate inferences concerning spatial variations (Bhat *et al.*, 2014), non-parametric rank-sum tests were employed including Spearman's correlation, Kruskal-Wallis and post-hoc Mann-Whitney U test. The Mann-Whitney U test was conducted using a Bonferroni correction of $\alpha=0.005$ was performed

to determine if parameters differ significantly based on the location of sites and, relative to the IDDS (Helsel and Hirsch, 1992).

Water Quality Index (WQI)

Sarkar *et al.*, (2006) defined the WQI as a rating technique that provides a composite assessment of the influence of a range of physicochemical parameters on overall quality of water. In the case of the IDDS, whilst comparison to the TWQR and the statistical analyses focuses on the potential contaminant status of individual parameters, the WQI provides the composite impact of the physicochemical loading at each of the five sampling sites.

A variety of methods are available for the determination of the WQI. The method selected for use in this study is the widely applied weighted arithmetic index proposed by Brown *et al.*, (1972). Numerous studies on water quality have utilized this method (inter alia, Balan *et al.*, 2012; Chauhan & Singh, 2010; Ramakrishnaiah *et al.*, 2009; Shweta & Satyendra, 2015). This method categorizes the quality of the water into relative cleanliness using a set of physicochemical parameters. For this study, the parameters utilized were pH, EC, TDS, Na, K, Ca, SO₄ and Cl. The WQI was computed using the procedure that follows. Initially, each of the parameters was weighted in accordance of relative importance:

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \quad (1)$$

Where, W_i is the relative weight; w_i is the weight of each parameter and n is the number of parameters. In the third step, a quality rating scale (q_i) for each parameter is assigned by dividing the concentration in each sample by its respective standard from the DWS TWQR guidelines, the result is multiplied by 100 (Eq 2):

$$q_i = [c_i / s_i] \times 100 \quad (2)$$

Where, q_i is the quality rating; C_i is the concentration of each chemical parameter in each water sample in mg/L and S_i is the TWQR standard for each chemical parameter in mg/L according to the guidelines of the DWS (1996).

To compute the WQI, a sub-index (SI) is first determined for each parameter, which is then used to calculate the WQI as per equation 3.

$$SI_i = W_i \times q_i \quad (3)$$

$$WQI = \sum SI \quad (4)$$

Where SI is the sub-index of i^{th} parameter; q is the quality rating based on the concentration of i^{th} parameter and n is the number of parameters.

Calculated SI and WQI are presented in Table 4. The collected water samples are classified into five different status categories (Table 5) varying from unsuitable for drinking to excellent, based on computed WQI values.

Results and discussion

Physiochemical Analysis

The physiochemical parameters of river water samples were benchmarked against the DWS Water Quality Guidelines for Aquatic Ecosystems. In the absence of a target water range (TWQR) in the aquatic ecosystem guideline, the domestic and agricultural water quality guideline was adopted to determine fitness for use. Table 2 below gives the values that fall below the standard as TWQR; values that are above the TWQR and below the chronic effect range (CEV) (these are within the ‘tolerable’ range); the CEV where effects are moderate to adverse and, the acute effect range (AER) with severe adverse acute effects. Below is a discussion of the physiochemical analyses with reference to Figure 3, Table 2, and statistical results in Table 3 and Figure 4.

The chloride results (Cl) indicated that 27% of the samples exceeded the TWQR, falling within the unacceptable CEV range, and the AEV range. Chloride fluctuations in surface water can result from various industrial processes, sewage effluent discharges and irrigation return flows (DWAF, 1996a). The electrical conductivity (EC) results indicated that 45% of the samples exceeded the TWQR and fell within the tolerable, chronic, and acute effect value ranges, the latter with elevated unacceptable limits. According to DWAF (1996a), electrical conductivity concentrations ranging from 150-300 mSm have a marked salty taste, as a result, this would not be used on the aesthetic grounds if other suppliers were available. Whilst no health effects

are noticeable at this range, health effects are noticeable at 300mSm and above. The increase in electrical conductivity is attributed to the iron-enriched leachate from the coal discard dump.

Fifty-five percent of the potassium (K) samples were within the TWQR and deemed acceptable however, 54% of the sodium results (Na) were in exceedance of the TWQR exhibiting extremely elevated levels. Metabolically sodium interacts with potassium and are most significant extracellular and intracellular cations that is vital for all living organisms (DWAF, 1996a) health effects are noticeable at sodium concentrations above 600mg/L. According to DWAF (1996a), the levels of sodium concentrations in the surface are generally low, however, in this study, significant sodium concentrations are noted.

Sixty-one percent of the aluminium (Al) samples exceeded the TWQR and ranged within the CEV and AEV ranges. According to DWAF (1996a), the interactions of aluminium is strongly influenced by the pH. Aluminium is found in soluble forms in acid mine drainage water and is among the principal particulates emitted from coal combustion. The elevated levels of bio-available aluminium in water are toxic to a variety of aquatic organisms (DWAF, 1996c). Whilst there is some uncertainty in terms of the toxicity levels, the effects are dependent on the species and life stage of the organism (DWAF, 1996).

Table 2: Percentage (%) composition of parameters tested for compliance against the Target Water Quality Ranges (TWQR).

Anions and Cations	% within DWS TWQR	% within the Tolerable Range	% within the Chronic effect Value	% within the Acute effect value
Cl	20	7	25	2
SO ₄	45	1	1	8
K	55	0	0	0
Na	6	9	24	21
Al	0	0	60	1
Ca	36	16	0	0
Cd	0	0	1	15
Co	0	0	0	0
Cr	0	0	0	55
Cu	0	0	0	55
Fe	25	33	2	1
Hg	0	0	0	45
Ni	46	0	0	0
Pb	1	0	0	27
Zn	0	0	3	33

DWAF (1996a, b, c, and d) Target water quality range (TWQR); the Tolerable Range (above TWQR & below Chronic effect value); Chronic effect range: moderate to adverse effects and, Acute effect range: severe adverse effects.

Cobalt (Co) was not detected and Sulphates (SO₄), Nickel (Ni), and Calcium (Ca), on the other hand, were within the TWQR and categorised into the acceptable range. Sixteen percent of the Cd results exceeded the TWQR and fell within the chronic and acute effect value ranges. Fifty-five percent of the copper (Cu) and chromium (Cr⁶⁺) samples exceeded the TWQR and exceeded the AEV. According to DWAF (1996c), 90% of all Cr values need to be within the TWQR to ensure the protection of the aquatic system, however, in exceedance, Cr exerts toxic effects at different concentrations among different aquatic biota. Iron concentrations were found to be within the TWQR and tolerable limit range and not considered a problem. Forty-five percent of the samples showed Hg concentrations that exceeded TWQR and within the AEV and above whilst 46% of the samples showed Ni concentrations that were within the TWQR. Whilst Cu and Cr had the highest exceedance of the AEV from all parameters tested, Pb and Zn are also considered problematic since 27% of the Pb samples and 36% of Zn concentrations exceeded the TWQR and fell within the chronic and acute effect range exhibiting extremely elevated levels.

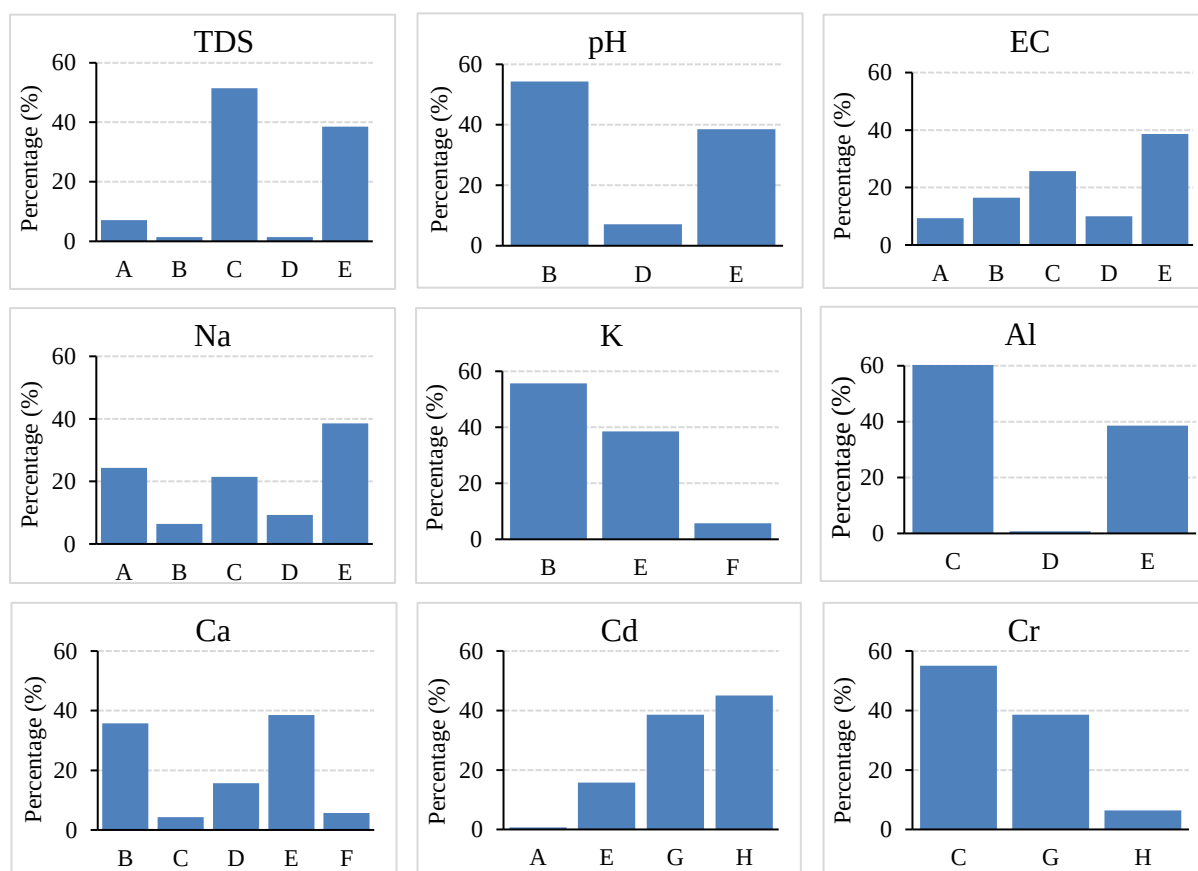


Figure 3: Graphical illustration of the percentage distribution of parameters of the river systems to the DWS target water quality ranges (DWS TWQR).

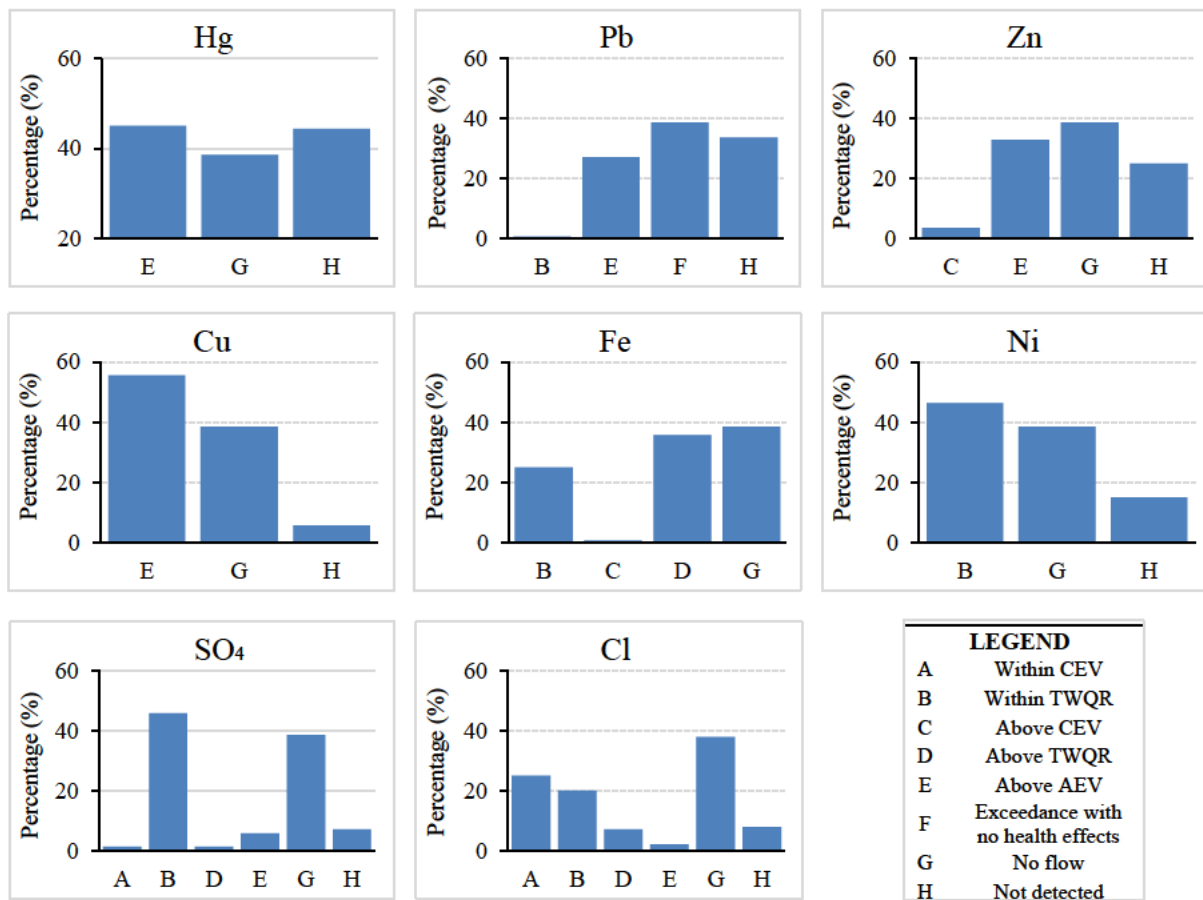
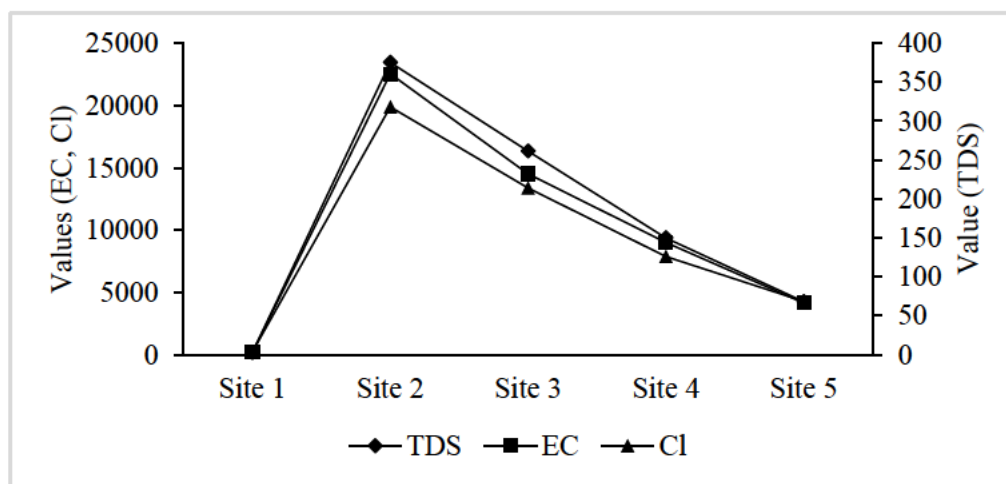


Figure 3 (continued): Graphical illustration of the percentage distribution of parameters of the river systems to the DWS target water quality ranges (DWS TWQR).



*All units in mg/L except for EC (mS/m).

Figure 4a: Mean values of EC, Cl and TDS across sites.

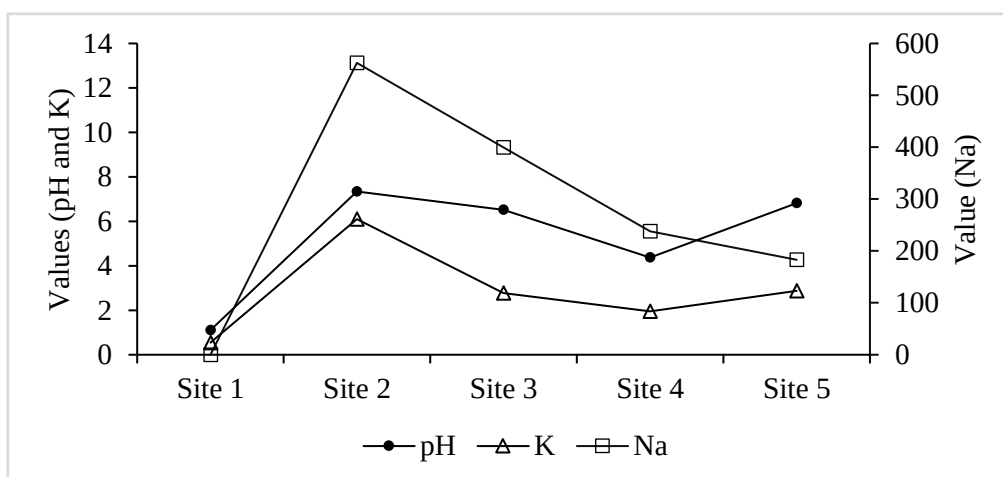


Figure 4b: Mean values of pH, K and Na across sites.

*All units in mg/L except for pH.

Six of the parameters were graphically plotted to show how they varied sequentially along the sites. The most obvious observation is that all parameters demonstrate a notable increase between site 1 (located upstream of the discard dump) and site 2 (located immediately downstream of the discard dump), followed by a general decrease from site 2 towards site 5, except for pH and TDS, although the latter does show an increase at site 2. This is strongly indicative of the impact of the leachates emanating from the IDDS upon the river system water quality. With increasing distance from the discard dump, there is a progressive decrease in the contaminant concentrations.

Statistical analysis of water quality parameters

A Spearman's rank correlation test indicated a statistically significant, strong positive relationship between Na and EC ($r = 0.911, p < 0.01$); Na and pH ($r = 0.782, p < 0.01$); pH and EC ($r = 0.891, p < 0.01$); pH and TDS ($r = 0.878, p < 0.01$); EC and TDS ($r = 0.967, p < 0.01$) and, TDS and Na ($r = 0.943, p < 0.01$). These results were expected as TDS influences the ions in the solution and consequently the EC.

With reference to Cl, the following significant, strong positive correlations were identified: Cl and pH ($r = 0.891, p < 0.01$); Cl and EC ($r = 0.888, p < 0.01$); Cl and Na ($r = 0.828, p < 0.01$), as well as Cl and K ($r = 0.889, p < 0.01$). K exhibited a strong correlation for parameters: K and pH ($r = 0.795, p < 0.01$); K and EC ($r = 0.870, p < 0.01$) and K and TDS ($r = 0.904, p < 0.01$). Sulphate had significant correlations with all elements: strong positive relationship

with Ni ($r = 0.465, p < 0.001$); Zn ($r = 0.446, p < 0.001$); Cu ($r = 0.610, p < 0.001$); and Al ($r = 0.547, p < 0.001$). Iron showed a positive, strong correlation with Ca ($r = 0.796, p < 0.001$); Al ($r = 0.922, p < 0.001$) and Cu ($r = 0.777, p < 0.001$). Calcium was shown to have a significantly strong positive relationship with Cr ($r = 0.890, p < 0.001$); Cu ($r = 0.857, p < 0.001$) and Hg ($r = 0.804, p < 0.001$). The analysis further showed a significantly strong positive relationship for Cu with several elements: Al ($r = 0.757, p < 0.001$), Cr ($r = 0.862, p < 0.001$), Fe ($r = 0.777, p < 0.001$), and Hg ($r = 0.727, p < 0.001$). In the same vein, strong, significantly positive relationships were identified for Cr and Al ($r = 0.755, p < 0.001$) as well as Cr and Cd ($r = 0.212, p < 0.05$). Nickel had a strong correlation with Pb, ($r = 0.713, p < 0.001$), Zn had a strong correlation with Ca ($r = 0.745, p < 0.001$) and with Cr^{6+} ($r = 0.725, p < 0.001$).

All physiochemical parameters were found to be statistically significant with a positive, strong correlation between pH, EC, TDS, Na, K and Cl. The mean concentrations of these parameters have been graphed per site and shown on Figure 4. Various processes from natural weathering and anthropogenic sources contribute to the addition of Na, K and Cl ions into natural water systems. The addition of dissolved ions above naturally occurring levels influences the physiochemical levels. This is likely due to surrounding activities in the area particularly the influence of the IDDS situated between sites 1 and 2.

The Kruskal-Wallis test was used to further characterise the distributional character of contaminants (Table 3). Results revealed a statistically significant difference for all physiochemical parameters such as pH, TDS, EC, K and Na and Cl ($p < 0.001$). A Mann-Whitney U test investigated the differences between each site which yielded multiple site pairs with significant differences (Table 3 and Table 4 respectively). pH was significantly different ($p < 0.005$) between site 1 and all other sites, shown by pairs (1-2), (1-3), (1-4), (1-5). EC was significantly different ($p < 0.005$) for site pairs (2-4) and (2-5) while TDS differences were found for site pairs (2-4) and (2-5). Cl had significant differences for site pairs ($p < 0.005$) (2-4) and (2-5). K was significantly different for pairs (2-3), (2-4) and (2-5) and Na was found to be different for (2-4).

Table 3: Results of the Kruskal-Wallis Test and Mann-Whitney U Tests showing differences in parameters among different sites.

Parameter	Kruskal-Wallis Test	Mann-Whitney U Test	Parameter	Kruskal-Wallis Test	Mann-Whitney U Test
	p value	Group p adj		p value	Group p adj
pH	<0.001**	1-2 <0.001*	Na	<0.001**	1-2 <0.001*
		1-3 <0.001*			1-3 <0.001*
		1-4 0.001*			1-4 0.001*
		1-5 <0.001*			1-5 <0.001*
		2-3 0.928			2-3 0.039
		2-4 0.110			2-4 0.001*
		2-5 0.178			2-5 <0.001*
		3-4 0.150			3-4 0.043
		3-5 0.226			3-5 0.017
		4-5 0.427			4-5 0.593
EC	<0.001**	1-2 <0.001*	K	<0.001**	1-2 <0.001*
		1-3 <0.001*			1-3 <0.001*
		1-4 0.001*			1-4 0.007*
		1-5 <0.001*			1-5 <0.001*
		2-3 0.052			2-3 <0.001*
		2-4 0.002*			2-4 <0.001*
		2-5 <0.001*			2-5 0.001*
		3-4 0.102			3-4 0.264
		3-5 0.066			3-5 0.661
		4-5 0.492			4-5 0.243
TDS	<0.001**	1-2 <0.001*	Cl	<0.001**	1-2 0.001*
		1-3 <0.001*			1-3 <0.001*
		1-4 0.001*			1-4 0.006*
		1-5 <0.001*			1-5 <0.001*
		2-3 0.089			2-3 0.082
		2-4 0.001*			2-4 0.003*
		2-5 <0.001*			2-5 0.001*
		3-4 0.038			3-4 0.042
		3-5 0.014			3-5 0.018
		4-5 0.483			4-5 0.300

Kruskal-Wallis test values with ‘***’ shows significance at $\alpha=0.05$.

Values with ‘*’ shows a significant difference between group pairs of the post hoc test using a Bonferroni adjusted $\alpha=0.005$.

Groups 1 to 5 represent each corresponding sampling site.

Table 3 (continued): Kruskal-Wallis Test and Mann-Whitney U Tests showing differences in parameters among different sites.

Parameter	Kruskal-Wallis Test	Mann-Whitney U Test	Parameter	Kruskal-Wallis Test	Mann-Whitney U Test
	p value	Group p adj		p value	Group p adj
Al	<0.001**	1-2 <0.001*	Hg	<0.001**	1-2 <0.001*
		1-3 0.001*			1-3 <0.001*
		1-4 0.48			1-4 0.065
		1-5 <0.001*			1-5 <0.001*
		2-3 0.053			2-3 0.056
		2-4 0.014			2-4 <0.001*
		2-5 0.025			2-5 0.286
		3-4 0.319			3-4 0.039
		3-5 <0.001*			3-5 0.339
		4-5 <0.001*			4-5 0.003*
Ca	<0.001**	1-2 <0.001*	Ni	<0.001**	1-2 <0.001*

		1-3	<0.001*			1-3	<0.001*
		1-4	0.009			1-4	0.014
		1-5	<0.001*			1-5	<0.001*
		2-3	0.197			2-3	0.347
		2-4	0.003*			2-4	0.067
		2-5	0.217			2-5	0.632
		3-4	0.071			3-4	0.290
		3-5	0.766			3-5	0.742
		4-5	0.026			4-5	0.214
Cd	0.923	1-2	0.669	Pb	0.024**	1-2	0.001*
		1-3	0.459			1-3	0.008
		1-4	0.459			1-4	0.016
		1-5	0.396			1-5	0.016
		2-3	0.758			2-3	0.516
		2-4	0.758			2-4	0.390
		2-5	0.682			2-5	0.096
		3-4	1.000			3-4	0.888
		3-5	0.083			3-5	0.398
		4-5	0.086			4-5	0.696
Cr	<0.001**	1-2	<0.001*	Zn	<0.001**	1-2	<0.001*
		1-3	<0.001*			1-3	0.023
		1-4	0.005*			1-4	0.410
		1-5	<0.001*			1-5	0.006
		2-3	0.442			2-3	0.047
		2-4	0.007			2-4	0.001*
		2-5	0.863			2-5	0.138
		3-4	0.065			3-4	0.116
		3-5	0.545			3-5	0.626
		4-5	0.015			4-5	0.046
Cu	<0.001**	1-2	<0.001*	SO₄	<0.001**	1-2	<0.001*
		1-3	<0.001*			1-3	<0.001*
		1-4	0.005*			1-4	0.012
		1-5	<0.001*			1-5	<0.001*
		2-3	0.396			2-3	0.061
		2-4	0.003*			2-4	0.001*
		2-5	0.058			2-5	0.003*
		3-4	0.034			3-4	0.071
		3-5	0.537			3-5	0.152
		4-5	0.044			4-5	0.520
Fe	<0.001**	1-2	<0.001*				
		1-3	<0.001*				
		1-4	0.033				
		1-5	<0.001*				
		2-3	0.173				
		2-4	0.008				
		2-5	0.340				
		3-4	0.156				
		3-5	0.051				
		4-5	0.001*				

Kruskal-Wallis test values with ‘***’ show significance at $\alpha=0.05$.

Values with ‘**’ show a significant difference between group pairs of the post hoc test using a Bonferroni adjusted $\alpha=0.005$. Groups 1 to 5 represent each corresponding sampling site.

A Kruskal-Wallis test revealed statistically significant differences for all metals including Al, Cr, Ca, Cu, Fe, Hg, Ni, Pb, SO₄ and Zn ($p < 0.05$), except for Cd ($p > 0.05$) which was not significantly different among the five sampling sites.

The Mann-Whitney U test identified the specific sites which showed significant differences. Ca, Cr and Ni were significantly different ($p < 0.005$) between site pairs, (1-2), (1-3) and (1-

5). A significant difference was found for Al, Hg, and SO₄ among five of the following site pairs, (1-2), (1-3), (1-5), (2-4), (4-5). Cu had significant differences for ($p < 0.005$) at sites: (1-2), (1-3), (1-4), (1-5), (2-4). Lastly, Pb had one site pair (1-2) which was found to be significantly different while Zn exhibited a significant difference for site pairs, (1-2) and (2-4).

Table 4: Summary results of Mann-Whitney U depicting significant differences between site pairs.

Site	1	2	3	4	5
1	-	pH, EC, TDS, Na, K, Cl, Al, Ca, Cr, Cu, Fe, Hg, Ni, Pb, Zn, SO ₄	pH, EC, TDS, Na, K, Cl, Al, Ca, Cr, Cu, Fe, Hg, Ni, SO ₄	pH, EC, TDS, Na, K, Cl, Cr, Cu	pH, EC, TDS, Na, K, Cl, Al, Ca, Cr, Cu, Fe, Hg, Ni, SO ₄
2		-	K	EC, TDS, Na, K, Cl, Ca, Cu, Hg, Zn, SO ₄	TDS, Na, K, Cl, EC, SO ₄
3			-		Al
4				-	Al, Fe, Hg
5					-

The table above highlights parameters which exhibited significant differences between each site combination. The site pair which had the greatest number of parameters exhibiting significant differences was between site 1 and all other sites. This is particularly stark between site 1 and site 2 with 16 parameters including pH, TDS, EC, K, Na, Cl, Al, Ca, Cr, Cu, Fe, Hg, Ni, Zn, Pb and SO₄. Site 1 is located upstream of the IDDS and so not directly impacted by the discard dump. This is especially true of the differences between sites 1 and 2, the latter being most immediately impacted by leachate from the discard dump. This is also evidence by the presence of ferric hydroxide (yellow boy) as observed during field investigations in site 2, this is an indication of acid mine drainage characteristics which has contributed to this result.

Site 1 and site 3 had 14 parameters which were significantly different as well as site 1 and site 5. This included pH, EC, TDS, Na, K, Cl, Al, Ca, Cr, Cu, Fe, Hg, Ni, SO₄ subsequently outlining the impact level on the aquatic system. Site 3 to site 4 was the only combination along the study area which yielded statistically significant differences for any of the parameters and may be related to natural attenuation. While there is a decrease of means between these sites

(Figure 4), there were occasions at site 4 when there was no flow due to prolonged winter dry periods. This indicates that parameter concentrations from site 1 to site 2 have a meaningful difference which could be a result of the adjacent environment at each site. Sites 3, 4 and 5 all had fewer parameters of significance, indicating that ions in solution may be inhibited or potentially experience dilution downstream. Marove *et al.* (2022), emphasize that coal discarded materials are naturally contaminated with inorganic constituents. A number of inorganic constituents that are referred to here have been incorporated in this study as listed above. Additionally, Vejahati *et al.* (2010), note that trace elements are available in the coal ash, indicating that the coal discard dump was impacted by instantaneous combustion. These trace elements were detected in varying concentrations through XRF analysis on the coal discarded material as detailed in a paper entitled: *The characterization of Acid Mine Drainage using Static Testing at the abandoned Indumeni Discard Dump Site, uThukela Water Management Area, KwaZulu-Natal, South Africa.*

Water Quality Index

Results of the WQI calculations in Table 4 and the WQI ratings are presented in Table 5 below.

Table 4: Summary of physiochemical water quality assessment, including the SI calculated values (Eq. 4) and the WQI (Eq. 5).

Parameters	DWS STDs	SITE 1	SITE 1 SI	SITE 2	SITE 2 SI	SITE 3	SITE 3 SI	SITE 4	SITE 4 SI	SITE 5	SITE 5 SI
pH	9.00	7.75	21.80	8.57	21.80	8.69	21.80	8.74	21.80	8.31	21.80
EC	70.00	17.32	1.73	423.39	42.38	317.88	31.82	287.97	28.83	81.33	8.14
TDS	450.00	1125.78	2.73	27361.39	66.28	21782.94	52.76	18718.24	45.34	5178.26	12.55
Na	100.00	90.44	4.44	656.26	32.19	532.91	26.14	475.49	23.32	222.57	10.92
K	50.00	4.91	0.96	7.76	1.52	4.08	0.80	4.56	0.90	3.65	0.72
Ca	32.00	24.41	11.69	45.89	21.98	50.58	24.23	27.66	13.25	20.97	10.04
SO ₄	200.00	1356.42	16.63	119.18	1.46	121.38	1.49	92.45	1.13	553.24	6.78
Cl	100.00	32.73	1.61	424.16	20.81	315.50	15.48	321.24	15.75	87.27	4.28
WQI			61.59		208.42		174.52		150.32		75.23

Table 5: Status categories of the WQI (Brown *et al.*, 1972).

WQI	STATUS OF THE WATER
1 - 25	Excellent
26 - 50	Good
51 - 75	Poor
77 - 100	Very poor
>100	Unfit for domestic use

The WQI enables an overall analysis of water quality and can be used in a variety of ways dependent on the use that the assessment is intended for. Its utility is in its ability to take into consideration a composite suite of parameters and provide a generic categorization of the water quality which can be used to assess the ability of a water resource to support aquatic biota or whether the overall quality poses any threat to other water uses (Akkaraboyina and Raju, 2012). From Table 4, the average WQI of S1 ranges between 61.59 (poor water quality) at Site 1 located upstream of the IDDS, to 208.42 at S2 (unfit for domestic use) immediately downstream of the discard dump site. It is clear from this result alone that the discard dump is contributing a significant amount of contaminants to the river system through leaching processes. Interestingly, there is an increase in water quality from Site 3 (WQI = 174.52) to Site 4 (WQI = 150.32) to Site 5 (WQI = 75.23). This is probably due to some sequestration of contaminants with increasing distance from the discard dump site. Nevertheless, the water quality at these sites is still unacceptably high, ranging from unfit for domestic use (S2, S3 and S4) to very poor (S1 and S5). Since the latter sites are located at some distance from the discard dump, other past and current land uses are thought to also have a role in the poor water quality. Additionally, this issue is linked to legacy impacts of surface and groundwater pollution emanating from the abandoned mines in this catchment. Hence follow-up studies that incorporate the role played by surrounding land-uses should be undertaken.

Conclusion

This study presents the research results into the water quality of river systems that flow adjacent to the IDDS in the Klip River Coalfields, KwaZulu-Natal, South Africa. Collected water

samples from five sampling sites over a period of 27 months and analysed for a broad range of elements, including heavy metals. Site 1 was located just upstream of the discard dump on the Biggarsgatspruit River and would not have been directly impacted by any leachate from the dump.

The water quality compliance levels for fitness of use indicated compliance and non-compliance levels to the DWS TWQR. Over the study period, the water quality of the river system was not fit for use as only six parameters, these include Fe (58%), K (55%), pH (54%), Ca (52%), SO₄ (46%), Ni (46%) complied with the DWS TWQR, and 11 parameters were in exceedance of the DWS TWQR that ranged within the chronic and acute effect value range. These include Al (61%), TDS (59%) Cr⁶⁺ (55%), Cu (55%), Na (54%), Hg (45%) EC (45%), Zn (36%), Pb (27%), Cl (27%) and Cd (16%).

The Kruskal-Wallis test and a Mann-Whitney U post-hoc test were performed to determine if parameters differ significantly based on the location of sites relative to the IDSS. There are significant, positive correlations between pH, EC, TDS, Na, K and Cl.

The mean concentrations of these parameters across sites (figure 4) clearly peak at site 2, the site immediately affected by the discard dump. Results of the Kruskal-Wallis test further characterised the distributional character of contaminants revealed statistically significant differences for all physio-chemical parameters such as pH, EC, TDS, Na, K and Cl ($p < 0.001$). The post-hoc Mann-Whitney U test was performed to further investigate the differences between each site which yielded multiple site pairs of parameters with significant differences. pH was significantly different between site 1 and all other sites; EC, TDS and Cl were significantly different for site pairs (2-4) and (2-5) while K was significantly different for pairs (2-3), (2-4) and (2-5) and Na was found to be different for (2-4). Further research is advised to identify the causes of these outcomes.

Results of the WQI assessment indicates the composite quality of the surface water sampled at the five sites is very poor, specifically the water quality at Site 2, just downstream of the IDSS is categorised as unfit for domestic purposes and is clearly indicates contamination from the dumpsite itself. Sample sites 3, and 4 are also categorised as unfit for domestic use. Although the actual coal discard dump in the vicinity of the resources does play a role in the pollution

contribution, it is not solely responsible for the pollution, but rather a contributor to the overall pollution issues.

The elevated levels of physiochemical and heavy metals have contributed to the polluted state of the river systems, resulting in the water quality being considered unfit for use and impacting the aquatic biota and environment. This situation observed from the assessment can be attributable to historical mining-related activities and inadequate mine water pollution control.

It is therefore recommended that further investigations be conducted, and that comprehensive mine water management control be established and implemented in this catchment area to protect water resources for the aquatic biota, livestock, domestic and agricultural use.

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Declaration

The authors declare no conflicting interest.

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Paper 2:

The characterization of Acid Mine Drainage using Static Testing at the abandoned Indumeni Discard Dump Site, uThukela Water Management Area, KwaZulu-Natal, South Africa.

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Abstract

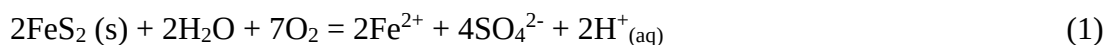
Acid mine drainage (AMD) from coal mining has caused serious environmental degradation worldwide. In South Africa, a key coal-producing area is located in the midlands of the KwaZulu-Natal province. Historical mining practices have left numerous unprotected coal discard dumps, many of which pose environmental risks through AMD production. The Indumeni Discard Dump Site (IDDS) of this area was studied in detail to assess its potential acid generation threat. Coal discard material from the site was analysed for mineralogy, metal composition, physicochemical character and acid generation potential using acid-base accounting methods (static testing). Results demonstrate that all of the discarded material from the site has positive acid-producing potential (+NAPP) ranging from 19.28 KgH₂SO₄ in the northern part of the dump to 92.13 KgH₂SO₄ near the centre of the site and 82.19 KgH₂SO₄ at the base of the site, and the site is geochemically classified as potentially acid-forming (PAF). Low organic carbon content points to possible long periods of leaching. XRF analysis identified 33 metals in the discarded material, with the highest concentrations measured in Ba (453.17ppm), Sr (360.80ppm) and Zr (127.08ppm); high concentrations of V and Ce (30 – 99 ppm) and moderate amounts (20 – 30 ppm) of Cr, Cu, Y and La. Leaching of these metals are likely to move to subsurface water as only a few were detected in surrounding surface water.

Introduction

The earliest accounts of human civilization often make reference to the transitions from purely agrarian lifestyles to more diverse capabilities due to the advances in the use of metallic implements (Christmann *et al.*, 2022). Mining activities have existed for centuries and provided the resources for tool manufacture (Stöllner, 2003; Coulson, 2012;). With the ages came new developments, innovations, and ever-expanding demand for a range of metals. Consequently, mining activities increased in scale and character to provide the resources required to drive economic development (Shengo, 2021; Zhou, 2024). As the need and demand for mined resources increased, so did the disruptions to the natural environment through mining operations (Bowell *et al.*, 2023). Not only did this manifest in terms of terrain and landscape changes, but also to surface and subsurface water contamination with knock-on impacts to biota

(Wolkersdorfer, and Mugova, 2022). The generation of mining waste such as mine tailings and discarded material has led to long-term environmental issues where these were not properly managed, posing potential serious health risks (Shengo, 2021; Araujo *et al.*, 2022). In South Africa, in the early period of mining and before the promulgation of environmental legislation, specifically the National Environmental Management Act of 1987 (NEMA), the mine discard material dumps were not subject to rehabilitation and restoration. Whilst the mining of an array of minerals contributed significantly to the development of the country, the abandoned operations and discard dumps have resulted in considerable environmental damage and continue to do so. As a result, acid mine drainage (AMD) has become a major problem in South Africa (Thompson, 1980; Fosso-Kankeu *et al.*, 2020; Moyo *et al.*, 2024).

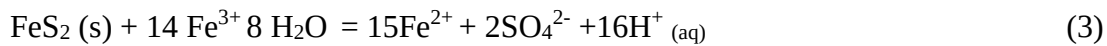
Consequently, acid mine drainage emanates from underground workings and pits, mine waste rock, tailings etc (Akcil and Koldas, 2006) and results from sulphide mineral oxidation, iron pyrite and other heavy metals when in direct exposure to water and oxygen (Druschel *et al.*, 2004). Though this process occurs naturally, mining can promote AMD by the increased quantities of the exposed sulphides. Additionally, bacteria occurring naturally can increase the production of AMD by breaking down the sulphide minerals (Skousen *et al.*, 2019). This exposure and the oxidative enhancement of the sulphide mineral pyrite (FeS₂) generate acidic and metal-rich waters (Druschel *et al.*, 2004) upon infiltration into mines and waste rock environments (Sharma *et al.*, 2020) and are further dependent on the mineralogy of the local environment (Akcil and Koldas, 2006), subsequently varying amounts of protons, metals and other harmful compounds / elements released to the environment (Dold, 2014). According to the Fosso-kankeu *et al.*, (2020), AMD is currently the second major environmental problem faced apart from global warming. This environmental hazard has not subsided after decades of research and continues to impact the environment (Rambabu *et al.*, 2020). The following chemical reactions below (equations 1-6) illustrate the acid mine drainage process (Banks *et al.*, 1996; Banks *et al.*, 1997; Dold, 2014; Stumm and Morgan, 1996; Weber *et al.*, 2004; Sharma *et al.*, 2020; and others) explain this complex reaction as follows:



(Pyrite + oxygen + water = ferrous iron +sulphate +acid)



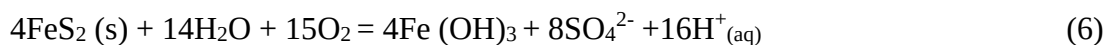
In equation 2 above partial oxidation of ferrous (Fe^{2+}) to ferric iron (Fe^{3+}) consumes some protons. This chemical reaction rate is increased by microbial activity (e.g., *Acidithiobacillus* spp. or *Leptospirillum* spp.) (Dold, 2014). The ferric iron could act as an electron acceptor for further oxidation of pyrite, or hydrolysis may occur. These processes further release protons as illustrated below.



Sharma *et al.* (2020), indicate the Fe (III) precipitates are referred to as “**yellowboy**”. This occurs as the pH increases, dissolved iron concentration decreases. Prabhakar and Lottermoser, (2015) note that the solubility of Fe^{3+} is restricted by precipitation of Fe^{3+} hydroxides [$\text{Fe}(\text{OH})_3$] and oxy-hydroxides (FeOOH). Subsequently an increase in pH of more than 3 triggers reactions 4 and 5 below.



Stumm and Morgan, (1996); Banks *et al.* (1996); Weber *et al.* (2004); Dold, (2014); Sharma *et al.* (2020); and others demonstrate the overall sequence of reactions below as acid-producing:



(Pyrite + Oxygen + Water = Iron Hydroxide + Sulphuric Acid)

In South Africa, much of the responsibility now falls on the governmental DWS to rehabilitate old, abandoned mines as well as mine discard dumps, often with limited resources. Hence the potential for continued environmental damage, particularly from acid mine drainage (AMD) and other contaminants leached from these sources, is a real threat. Concomitantly, and despite the regulatory power of the new legislation, of the National Water Act (Act 36 of 1998) and the Minerals and Petroleum Resources Development Act 28 of 2002, many abandoned mines

remain unrehabilitated and the possibility of pollution episodes from abandoned and currently operational mines is always a threat and requires continuous monitoring.

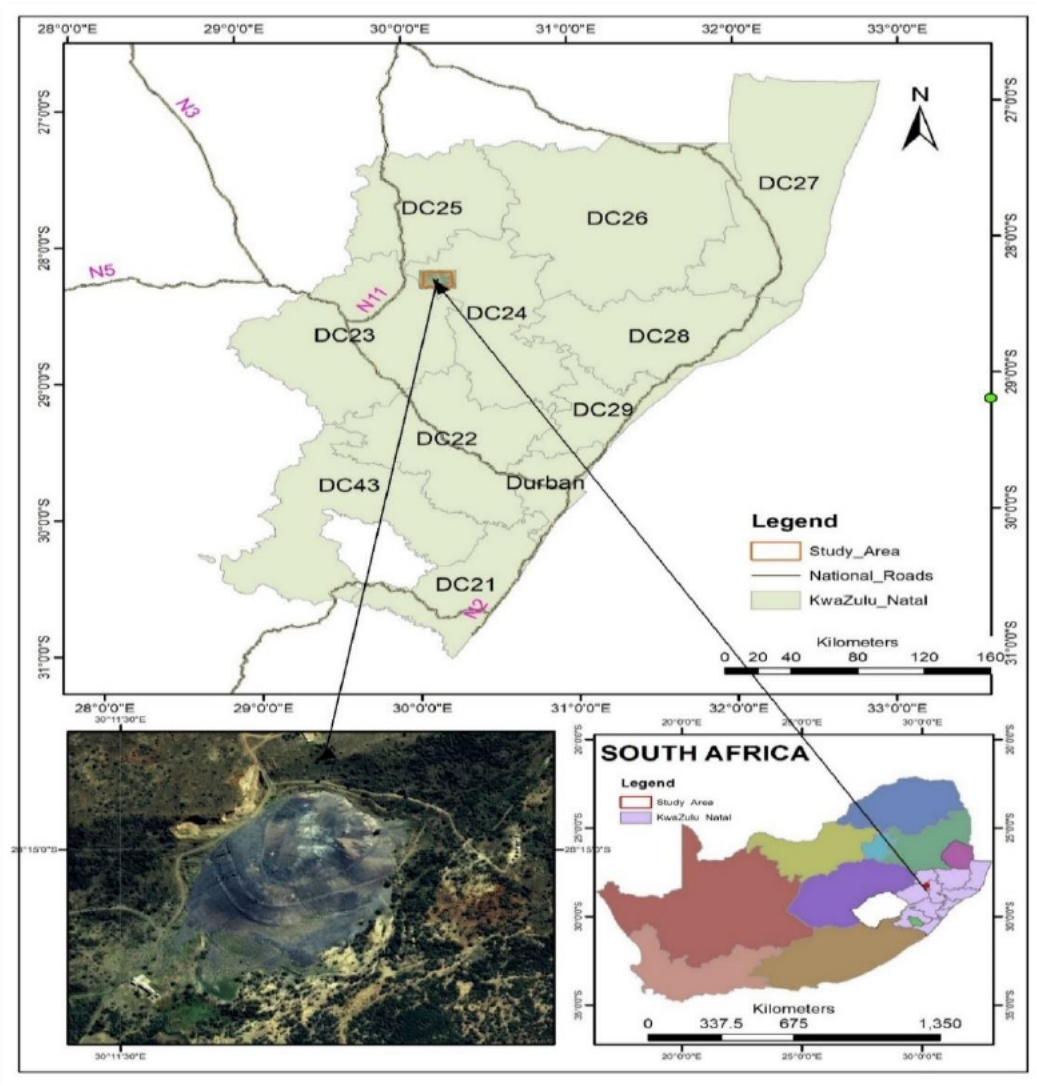
In this paper, an acid-base accounting (ABA) assessment of the mine tailings from a large, abandoned discard dump, the Indumeni discard dump site (IDDS) is made to evaluate the potential for AMD generation and the possible implications this would have on the surrounding receiving environment, particularly the adjacent river system, the Biggarsgat River. Acid-base accounting (ABA) is a widely used method for determining the potential for the generation of AMD. ABA is based on assessing the potential of mined materials for generating acidic or basic conditions and this is related to the mineralogical composition of the discarded material (Skousen *et al.*, 2001; Skousen *et al.*, 2022; Mafra *et al.*, 2022; Yassir and Sana, 2024). Yassir and Sana (2024) note that ABA is valuable in that it facilitates the predicting environmental impacts of mine discarded material and this, in turn, aids in the development of appropriate mitigation measures to counter potential harmful impacts of AMD.

Aim and objectives: The aim of this paper is to predict the generation of acid mine drainage potential and impacts from the abandoned coal discard dump on the surrounding water resources. The objective of the study is to determine the acid producing potential and impact of acid mine drainage using mineralogy, metal composition, physicochemical character and acid-base accounting methods (static testing) as presently there exists a knowledge gap on the impacts of acid mine drainage prediction from abandoned coal mines in northern KwaZulu-Natal.

Study site

South Africa is subdivided into 9 provinces (Figure 1), each of which is subdivided into District Municipalities. The latter are further subdivided into Local Municipalities. In KwaZulu-Natal, coal fields are located in its northern region. The study site, the IDDS, is located in this area and specifically within the Endumeni Local Municipality, one of four local municipalities within the uMzinyathi District Municipality. In terms of water management, the Department of Water and Sanitation (DWS) has demarcated Water Management Areas (WMA). The uMzinyathi District Municipality is located within the uThukela Water Management Area

(UDM, 2016), (presently referred to as the Pongola to Mtamvuma water management area) one of the largest in the province. The potential contamination of water resources within the catchment area from abandoned discard dumps as well as ongoing coal mining activities is one of the primary reasons for conducting this study. The IDDS, together with other such abandoned discard dumps in the area, has been of concern to the DWS due to its large size and the fact that it was created at a time when little to no attention was given to possible future environmental impacts. The responsibility of the water pollution control and abandoned mines prevention prior to 1956 (the promulgation of the Water Act, 1956) at this site remains the



responsibility of the state, this was according to the agreement of responsibility between the

Figure 1: Location of study area within uMzinyathi District in KZN, South Africa.
(Adopted from Govender S, 2025 submitted for publication).

then Department of Water Affairs and the Chamber of Commerce as well as under certain conditions, for mines abandoned prior 1976 (the promulgation of regulation R287 pertaining to water management on mines in terms of Section 26 of the Water Act), (DWS, 2014); however, mine water pollution emanating from this site continues to date.

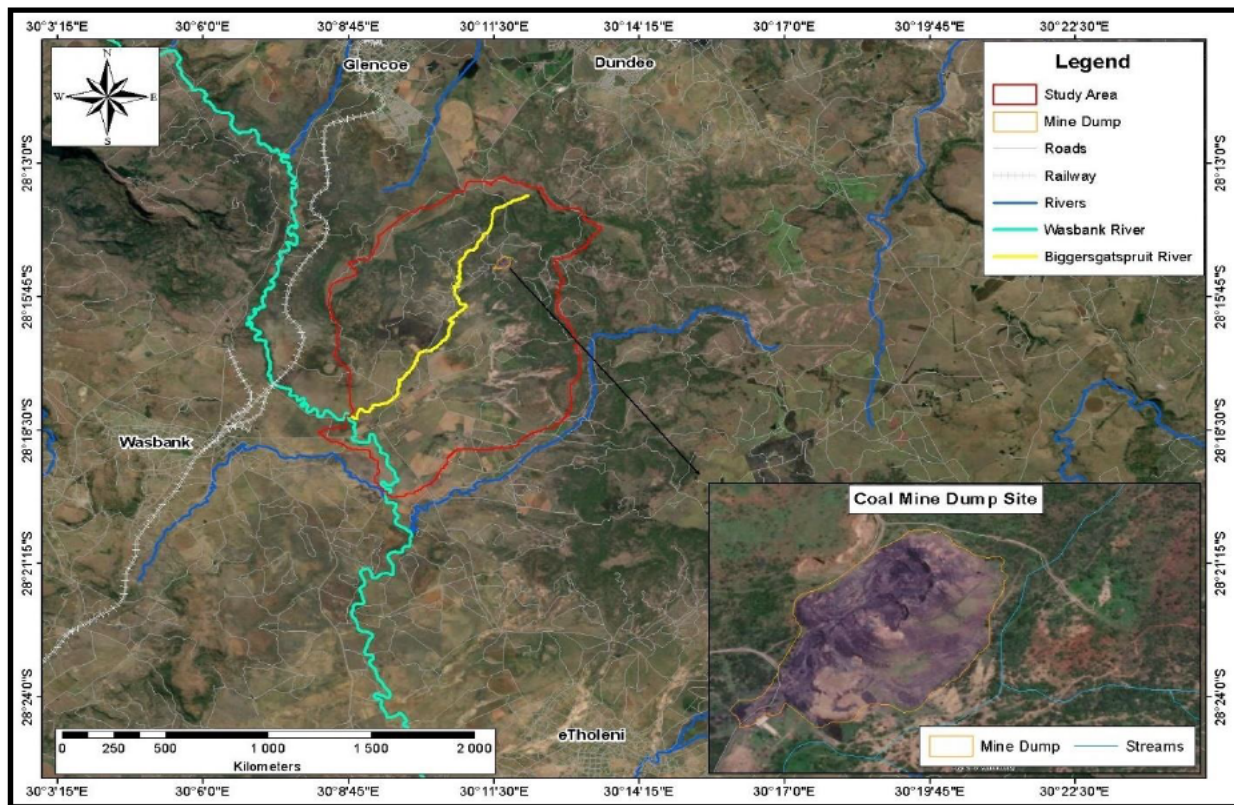


Figure 2: Location of Indumeni discard dump in the study area within uMzinyathi District in KZN, South Africa. (Map drawn by Namitha Singh, 2021). The IDDS is shown on the Google Earth image on the lower right.

Adjacent and slightly downstream of the IDDS, a pollution control dam was constructed by the DWS to aid in mitigating possible downstream contamination. In the past, regular monitoring of the dam water quality was undertaken by the DWS, currently, there exists a gap in monitoring water quality of the pollution control dam and affected water resources. Consequently, concern about the AMD generation and negative effects on subsurface water as

well as downstream ecosystems have provided the impetus to undertake a comprehensive assessment of the acid-base accounting (ABA) of the materials comprising the IDDS using established methodologies. Based on results, sustainable mining practice and possible strategies in mitigating the environmental impact of these mine tailings will be developed and presented in a separate paper.

Description of the IDDS

The IDDS is located at 28°15'8.47"S 30°11'30.66"E approximately 10 km to the SW of the town of Dundee (Figure 2). The discard dump is situated on a fairly flat surface excavated into a hillslope. Hence, the slope elevation at the upper limits of the dump is 1200m above mean sea level (amsl) whilst the ground elevation at the lower portion of the dump is 1160m amsl. Prior to 2016, the IDDS covered an area of approximately 11Ha at its base with an upper surface area of approximately 3.5Ha and with a maximum elevation of 19m. According to DWS calculations, the volume of material contained amounted to 1 506 507 m³ with an estimated mass of 1 657 157.7 metric tons. Since 2017 secondary mining of dumpsite commenced and this has continued to date.

Geology of Study Area

The geology comprises of sedimentary rocks that form part of Vryheid Formation, Eccra Group (Green *et al.*, 2012). This was deposited during gradual transformation from marine to non-marine conditions leading to the formation of extensive coal deposits within a mudstone–sandstone succession (Green *et al.*, 2012), that comprise of bituminous and anthracite coal.

Materials and Methods

Field Sampling

Discard coal samples were collected from five sites located on the IDDS (Figures 2 and 3). Samples were extracted using a Dutch soil auger and a spade and, both the samples and their sites of extraction were logged. An equivalent composition of all coal discard samples (C1-C5) was taken and formed the composite sample. Since some combustion of the surface material of the discard dump had occurred variously over time, the depth at which samples were taken varied (near surface to <1,5m) depending on the auger encountering discard material unaffected

by any combustion. Samples, weighing approximately 2.5 kg each, were transferred to the laboratory for a series of follow-on analyses.

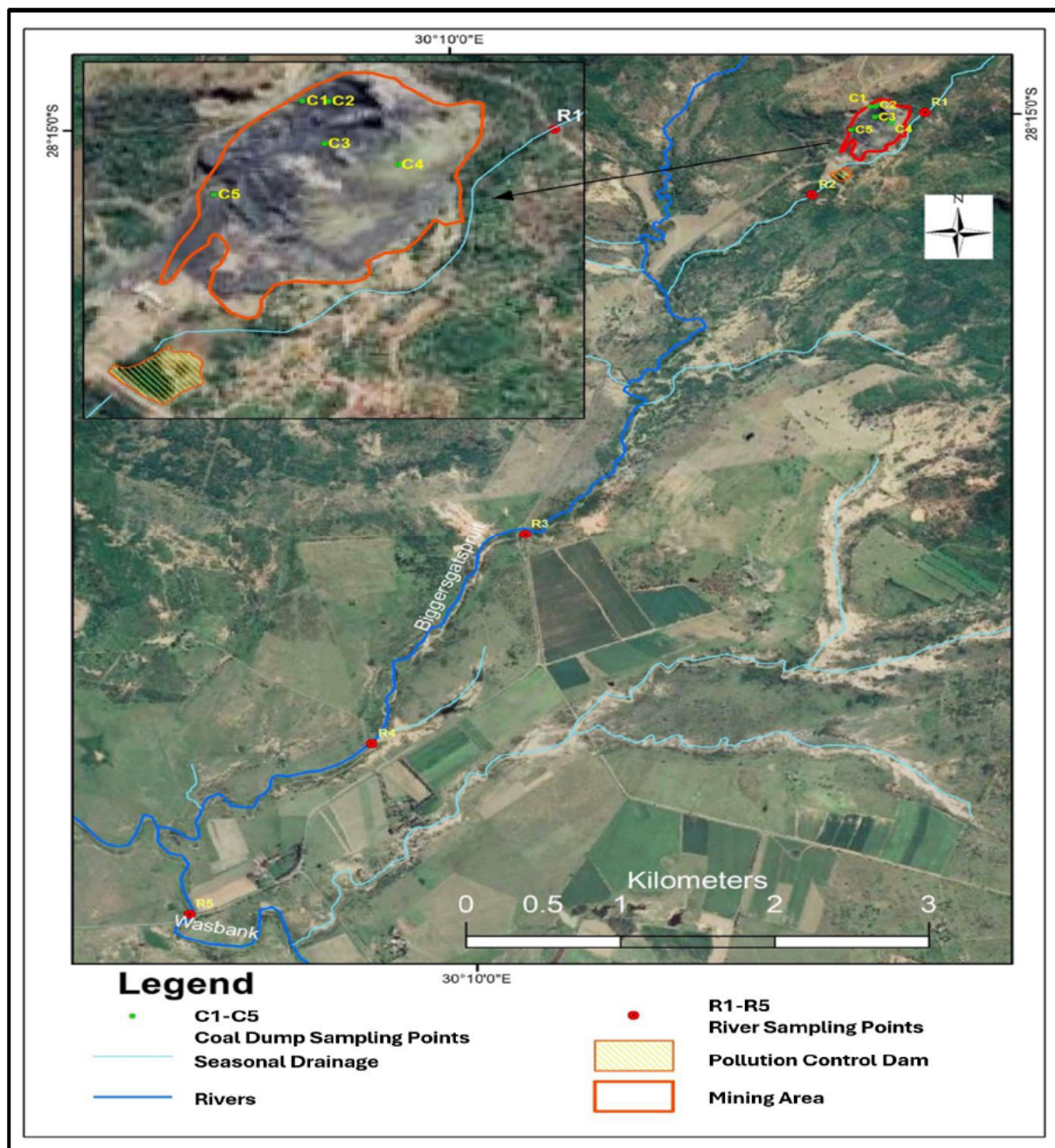


Figure 3. The study area showing sampling sites on the Indumeni coal discard dump and, the Biggersgatspruit and Wasbank Rivers (Adopted from Govender S, 2025 submitted for publication).

Laboratory Analyses

In the soil lab of the University of KwaZulu-Natal, a subset (approximately 1kg) of each of the samples was disaggregated, homogenized, pulverized and sub-divided into samples. The samples were oven-dried for 24hr at 110°C. The sulphur and carbon analyses of a portion of the pulverized discarded coal were conducted using the CHNS Elemental analyser. The sulfate concentration was quantified using the Hanna's solid-state combination sulphate ion-selective electrode (Hanna Instruments®).

The following geochemical investigative tests were conducted on the coal discard samples as part of the initial acid mine drainage assessment: electrical conductivity (EC) and pH; total sulphur and carbon analysis; acid neutralising capacity (ANC) test; net acid-producing potential (NAPP); the single addition net acid generation (NAG) test and the sequential NAG test.

pH and Electrical Conductivity (EC) of the Coal Discard Slurry

Paste pH indicates the immediate pH sample characteristics when mixed with water, be it acidic or alkaline, but not the total acid generating and alkalinity potential (Weber *et al.*, 2006). The paste pH/EC analysis was determined by equilibrating the sample in deionised water for approximately 12 hours at a solid-to-water ratio of 1:2 (w/w) thereafter measuring pH and EC. This analysis indicated the salinity and acidity of the waste material when initially exposed in the mine discard dump. Twenty-five grams (25g) of pulverised (<75µm) discarded coal sample was placed in a beaker and 50 g of distilled water was gradually added while continuously stirring to form a slurry. The slurry was allowed to stand for 12 hours before the EC and pH measurements were taken (Smart *et al.*, 2002).

Total Sulphur and Carbon Analysis

The sulphur and carbon analyses were conducted using the Carbon Hydrogen Nitrogen Sulphur (CHNS), Elemental analyser. A portion of the coal discard sample (dry and pulverized) was placed into a combustion chamber and the percentage of hydrogen, carbon, sulphur and nitrogen was obtained. For this research, the percentages of carbon and sulphur were used.

Acid Neutralising Capacity (ANC) Test

The acid neutralizing capacity (ANC) of the coal discard samples was determined using a modified Sobek method (Sobek *et al.*, 1978). An aliquot of each of the five samples (0.5g) was first assigned a “fizz rating” to determine the concentration and amount of acid used in the analysis. For each finely ground sample, standardised hydrochloric acid (HCl) of known amount was added to the finely ground coal samples of accurate weight, allowing time to react with heating (Smart *et al.*, 2002). Measurement of the pH of the mixture was taken using a Microprocessor pH meter. The pH values were greater than 1.5 for samples 3 and 4, (with a fizz rating of 2) and additional acid was required (the exception occurs when the test is run at a 0-fizz rating). The mixture was then back titrated with standardised NaOH to determine the amount of unreacted HCl. The calculation of the amount of acid consumed by reaction was calculated and expressed in the same units as the MPA (kg H₂SO₄/t) (Sobek *et al.*, 1978; Smart *et al.*, 2002). The ANC was then calculated as:

$$\text{ANC} = [\text{Y} \times \text{MHCl} / \text{wt}] \times \text{C} \quad (7)$$

Where: Y = (Vol. of HCl added) - (Vol. of NaOH titrated x B); B = (Vol. of HCl in blank) / (Vol. of NaOH titrated in blank); MHCl = Molarity of HCl; wt = Sample weight in grams; C = Conversion factor (49.0 to calculate kg H₂SO₄/t); (C=5.0 to calculate % CaCO₃ equivalent)

Samples 1, 2 and 5 were within a fizz rating of zero and samples 3 and 4 were within a fizz rating 2. Samples with an ANC result within the specified fizz rating range at which the test was conducted, indicated that a correct amount of acid had been added. Analyses were repeated at a different fizz rating for results that were outside of the upper and lower limits of the ANC.

Net Acid Producing Potential (NAPP) calculation (based on Sulphur and ANC values)

The net acid-producing potential (NAPP) was used to determine the potential of the mine discard sample to potentially generate acid drainage. This value of the NAPP signifies the balance between the capacity of a sample to generate acid (Maximum Potential Acidity-MPA)

and its capacity to neutralise acid (ANC) (Sobek *et al.*, 1978; Smart *et al.*, 2002). The NAPP is expressed in units of kg H₂SO₄/t. Following the above, the NAPP was then calculated using the following:

$$\text{NAPP} = \text{MPA} - \text{ANC} \quad (8)$$

The NAPP is negative if the MPA is less than the ANC, indicating that the sample may have sufficient ANC to prevent acid generation. If the NAPP is positive, the MPA exceeds the ANC which indicates that the material may be acid-generating (Sobek *et al.*, 1978; Smart *et al.*, 2002).

Single Addition Net Acid Generation (NAG) test

Whilst acid generation and acid neutralization may occur concurrently, the net amount of acid generated (NAG) was assessed (in kg H₂SO₄/t) to assess the risk involved. A pulverised sample (2.5 g) was reacted with 250 ml of 15% H₂O₂ in a conical flask in a fume hood. The sample reaction was completed at boiling when effervescence stopped. The pH (NAGpH) of the solution was then recorded. The solution was titrated to pH 4.5 and 7.0 with NaOH (concentration based on NAGpH - when NAGpH was > 2 titration with 0.10 M NaOH was adopted and when NAGpH was = 2 titration with 0.50 M NaOH was adopted. The NAG (in H₂SO₄/t) was then calculated as:

$$\text{NAG} = (49 \times V \times M)/W \quad (9)$$

Where: V = volume of NaOH; M = concentration of NaOH; W = weight of sample reacted (g)

A multistage sequential NAG test, as per Smart *et al.*, (2002) similar to the NAG test above was further performed to prevent any incomplete oxidation and to obtain the maximum NAG value for samples 2 to 5, which had NAG/MPA ratios <5. In this process, the sample treated with hydrogen peroxide was allowed to react for two hours, then heated until effervescence stopped. The sample was cooled, and the pH and EC was recorded. The sample was filtered, and the NAG liquor retained for titration with NaOH to pH 4.5 and 7.0, based on NAGpH (0.10M NaOH when NAGpH was >2; and 0.50M NaOH when NAGpH was =2). Following this, the NAG was calculated as per equation 3 above.

Results and Discussion

Acid-base accounting of coal discard material makes use of static procedures that seek to assess the balance between acid generation capacity of the material and its inherent acid neutralization (Skousen *et al.*, 2002; Smart *et al.*, 2002). The former generally involves the sulphide mineral oxidation and the latter the dissolution of alkaline carbonates, displacement of exchangeable bases and weathering of silicates (Smart *et al.*, 2002). Determination of the important physicochemical parameters is an important part of the process. These were analysed and are presented in Table 1 together with the acid generation and acid neutralization data. The geochemical classification of all samples was grouped as potentially acid-forming.

Table 1: Geochemical characterisation of the IDDS (Samples S1 to S5 and the composite sample) using static test procedures.

Parameter / Geochemical analysis	S1	S2	S3	S4	S5	Composite
pH	1.37	2.99	6.98	5.38	3.09	4.35
Electrical Conductivity (EC) (mS/m)	14.54	2.63	2.69	2.32	3.41	4.46
Total Sulphur %	1.764	2.93	1.82	2.64	2.50	2.33
Total Carbon %	44	47.02	60.84	34.68	40.21	45.35
MPA	53.97	89.81	55.44	80.96	76.56	71.32
ANC% KgH ₂ SO ₄ /t	-1.59	-0.98	18.37	31.84	-1.05	-144.66
ANC% CaCO ₃	-0.16	-0.1	1.87	3.25	-1.01	-11.7
NAPP KgH ₂ SO ₄ /t	57.64	92.13	38.42	63.32	82.19	185.99
NAGpH	2.00	2.83	3.24	2.93	2.09	2.62
NAG _{4.5} KgH ₂ SO ₄	119.5	18.62	6.54	10.74	31.24	18.22
NAG _{7.0} KgH ₂ SO ₄	225.40	26.30	23.48	37.19	48.92	34.69
NAG/NAPP	2.07	0.2	0.17	0.16	0.38	0.09
Depth of Sample	0-30cm	30-80cm	1 m	1.5m	+25m	Combination of S1 to S5 depths
Geochemical Class	PAF	PAF	PAF	PAF	PAF	PAF

MPA-Maximum potential acidity; ANC-Acid neutralisation capacity; NAPP-Net acid-producing potential; NAG-Net acid generation. Units in Kg H₂SO₄ (sulphuric acid/hydrogen sulphate); PAF-Potentially acid-forming.

Total carbon analysis of the samples yielded contents of 34.68% to 60.84%. This places S2 and S3 in the bituminous class whilst the other three are classed as sub-bituminous. This is to be expected in a discard dump where various grades of material have been stock-piled. It is likely that the organic carbon content of the samples will be relatively low given the long period of leaching action that the dump material has undergone.

All samples contained significant amounts of sulphur (>1%) although this has not automatically translated into high acidic purely by virtue of the pH. It is also recognised that the using total sulphur for MPA estimation is a conservative approach since sulphur occurs in forms other than pyrite as well and sulphate sulphur is a non-acid generating form of sulphur. Further, some sulphites may be present as minerals other than pyrite – for instance, as galena (PbS), sphalerite (ZnS), chalcocite (Cu₂S) or covellite (CuS) (AMIRA, 2002).

XRD Analysis

Coal samples (1 to 5) and an aliquot of the composite sample were investigated for chemical and crystallographic phase as well as crystallinity determination using X-ray diffraction. The Composite, Sample 2, Sample 4, and Sample 5 were found to contain quartz, kaolinite/dickite, illite/muscovite and gypsum while both Samples 1 and 3 contained quartz, kaolinite/dickite and gypsum. The highest crystallinity index observed is ~74% with Samples 1 and 3 showing the highest amorphous content (lowest crystallinity index). This may contribute to the neutralising capacity with the presence of gypsum in addition to the amorphous content. Quartz is simply SiO₂ and Gypsum is Calcium sulphate Dihydrate (CaSO₄ · 2H₂O). Both Kaolinite and Dickite are clay minerals with the same chemical formula (Al₂Si₂O₅(OH)₄) but different structures, the latter being a phyllosilicate clay mineral and a polymorph. This analysis shows that the detrital material incorporated into the discarded coal is unlikely to generate additional acidity. No pyrite or other acid-generating minerals were detected, and this is assumed to be a consequence of the advanced state of chemical decomposition of these minerals.

Metal Composition

A comprehensive analysis of the metal composition of a composite of the coal samples was also undertaken using ICP-MS to better appreciate the potential toxicity of any leachate from

the IDDS. Results of the metal analyses of the coal samples revealed of the presence of thirty-three metals as shown in Table 2 below. Prior studies on the mineralogy and geochemistry of coal have confirmed the presence of a wide range of metals within coal of various grades. Whilst sequential extraction techniques can aid the identification of the metal presence and their abundance, such investigation did not form part of the suite of analyses carried out in this study.

Table 2: Summarised mean metal composition (ppm) of a composite of the five coal discard samples.

Sc	V	Cr	Co	Ni	Cu	Zn	Rb	Sr	Y	Zr
8,00	39,82	26,36	10,18	12,50	23,25	16,66	28,91	360,80	20,46	127,08
Nb	Mo	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd
8,17	2,05	1,87	453,17	23,88	46,57	5,27	19,33	3,58	0,72	3,34
Tb	Dy	Ho	Er	Yb	Lu	Hf	Ta	Pb	Th	U
0,54	3,05	0,66	1,84	1,80	0,28	3,15	0,58	13,58	8,40	2,53

The composite sample (S1 to S5) contained very high amounts of Ba (453.17ppm), Sr (360.80ppm) and Zr (127.08ppm); moderately high amounts of V and Ce (30 – 99ppm); moderate amounts (20 – 30ppm) of Cr, Cu, Y and La; and, low Sc, Co, Ni, Rb, Zn, Y, Nb, Mo, La, Pr, Nd, Sm, Eu, Ho, Gd, Tb, Dy, Er, Yb, Lu, Hf, Ta, Th, Pb and U.

The concentration of ⁸⁷Sr in geologic materials tends to increase over long time scales (Spivak-Birndorf *et al.*, 2012). Sr, together with several of the other metals found in the composite coal sample and similar metals present in coal ash after combustion is known to be readily mobilized and biogeochemically available (Hurst *et al.*, 1991; 1993). Sr is a trace element in coal with an average concentration of about 100 mg/kg (Swaine, 1990; Spivak-Birndorf *et al.*, 2012). The exceptionally high amount of Sr found in the discarded coal composite sample points indicates relatively long ageing and, in turn, possible further long-term leaching to, and contamination of, surrounding water resources. The possible health effects with reference to excess Sr are related to the similarity of the latter to Ca and Mg and its possible replacement in bone tissue leading to bone cancers (DWS, 1996).

Cr, especially Cr (IV), may be found in low concentrations in aquatic systems (<0.1 mg/L). It can be toxic at levels over 5mg/L and since the composite discard sample has over 26ppm, its concentration in surrounding water bodies will require monitoring.

High Cu (>200mg/L) can be very detrimental, however the concentration detected is relatively low. Zn displays a similar pattern to Cu. Whilst V is naturally low in water (<0.1mg/L) the discard coal contains close to 40mg/L. Given that concentrations of >1mg/L in water has detrimental effects on respiratory functions, continuous monitoring of the potentially impacted water resources must be regularly checked. Pb, which is toxic at >50 mg/L also requires monitoring in adjacent water resources.

Trace element partitioning during coal combustion studies indicate that Ba, Be, Cr, Co, Sr, Mo, Pb, and Zn are the main elements that readily accumulate in coal ash (Vejahati *et al.*, 2010). Ba, Ca, Mg, Na and Sr decrease in concentration with coal rank (Lindahl and Finkelman, 1986; Swaine, and Goodarzi, 2013). High levels of Ba in drinking water can result in several health impacts with the most serious being the negative impacts to the urinary system (DWAf, 1996). However, Ba is fairly easily removed in water treatment. Zr on the other hand, has detrimental impacts to biota in the natural environment and should be kept below contamination levels in water systems. Both V and Ce occur in high concentrations in the composite coal and are a danger to the natural environment. Minor and trace elements that are water-insoluble or only very slightly water-soluble are Cr, Cu, Mn, Pb, Ti, and Zn (Spivak-Birndorf *et al.*, 2012). These elements are associated with more refractory phases in coal, such as clay minerals, phosphates, and other detrital minerals (Swaine, 1990; Izquierdo *et al.*, 2011) that are thought to partly transform into aluminosilicate glass and other compounds during combustion (Mattigod *et al.*, 1990; Spivak-Birndorf *et al.*, 2012).

As coal matures, some organic matter is destroyed and restructured as coal matures, causing the release and potential leaching of associated inorganic elements (Lindahl and Finkelman, 1986). Given the broad range of metals present in the composite sample, the potential exists for their gradual release in leachate. Subsequent leachate mobility into groundwater or into the

surface water will lead to contamination of these resources, hence regular monitoring over the long-term is a requisite to assess any further impacts.

Water quality sampling was conducted for the rivers adjacent to the IDDS and the results of this study are presented more comprehensively in a related paper entitled '*An Assessment of the impacts of the Indumeni coal discard dump on the Water Quality of Biggarsgatspruit, Wasbank, KwaZulu-Natal, South Africa*'. In this study, water samples were taken from five (5) sites along the Biggarsgat and Wasbank River over a 28-month period extending from 20 November 2017 (spring sample) to 18 February 2020 (summer sample). The samples were analyzed for physicochemical and heavy metal parameters. Interestingly, very few of the metals detected in the composite discard sample were detected in the rivers adjacent to the IDDS. Those detected include Cu, Cr (VI), Ni, Pb and Zn. Results showed that 78 of 140 samples or 55% of the samples contained Cu concentrations that exceeded the DWS Target Water Quality Requirement (TWQR). Since the rivers tend to run dry in the winter season, much of the balance of the sampling months yielded no water and hence no data. In like vein, 77 of 140 samples contained Cr (VI) that were above the TWQR for Cr. Of the available data for Ni, all samples were found to be within the TWQR whilst 38 and 46 of 140 samples exceeded the TWQR for Pb and Zn respectively. These results attest to the fact that not much of the leached metals from the coal discard actually reach the surface river system and may more likely be leached vertically to groundwater. However, further research needs to be conducted on the ground water quality to verify this assertion.

Acid Generation

The mechanism of acidogenesis or acid generation has been widely studied (e.g. Nordstrom *et al.*, 2000; Kumar *et al.*, 2024; Moyo *et al.*, 2024, Acharya *et al.*, 2020). This process leads to increased concentrations of sulphates and metals and the precipitation of iron oxides and hydroxides. The acid generation process is commonly demonstrated using pyrite oxidation, one of the most ubiquitous sulphide-bearing minerals in coal.

In this study, all samples had a positive net Acid Producing Potential (NAPP) value, Net Acid Generation (NAG) value of more than 5KgH₂SO₄/t and all samples were geochemically

classified to be Potentially Acid Forming (PAF) (Figure 4) including the composite sample and, S3, which exhibited a pH close to neutral. S4 has moderate acidity whilst the rest of the samples are highly acidic. All samples accordingly also demonstrate low carbonate content and, where some carbonates are present (S3 and S4), the ameliorative effect on reducing acidity is evident. In the case of S1, the high acidity is aided by the presence of sulphur and a relatively high EC. The NAPP ranged from 57.64 KgH₂SO₄/t in the northern part of the dump to 92.13 KgH₂SO₄/t at S2 near the centre of the site. Interestingly, Site S5 taken at the base of the stockpile and representing the ‘freshest’ sample, recorded a NAPP of 82.19 KgH₂SO₄/t. The ANC of S3 (17.64; 1.875% CaCO₃) and S4 (31.85; 3.25% CaCO₃) would have aided in neutralizing some of the NAPP for these two sites. The NAG values ranged from 119.5 KgH₂SO₄/t. (S1) to 6.54 KgH₂SO₄/t. (S3), with S5 being 31.24. Sample S1 NAG value was higher than the NAPP value for S1. According to Pope *et al.* (2010), a NAG value higher than the NAPP value indicates that organic content reacted with sample oxidation and produced titratable organic acids. Samples containing organic material as little as 3% could significantly impact the NAG result (Pope *et al.*, 2010). This is evident in samples S1 to S5, which yielded high organic matter, and the total carbon percentage ranged from 40.21% to 60.84%. The combination of the NAG and NAPP tests proved to be a better reflection of the site acid mine potential.

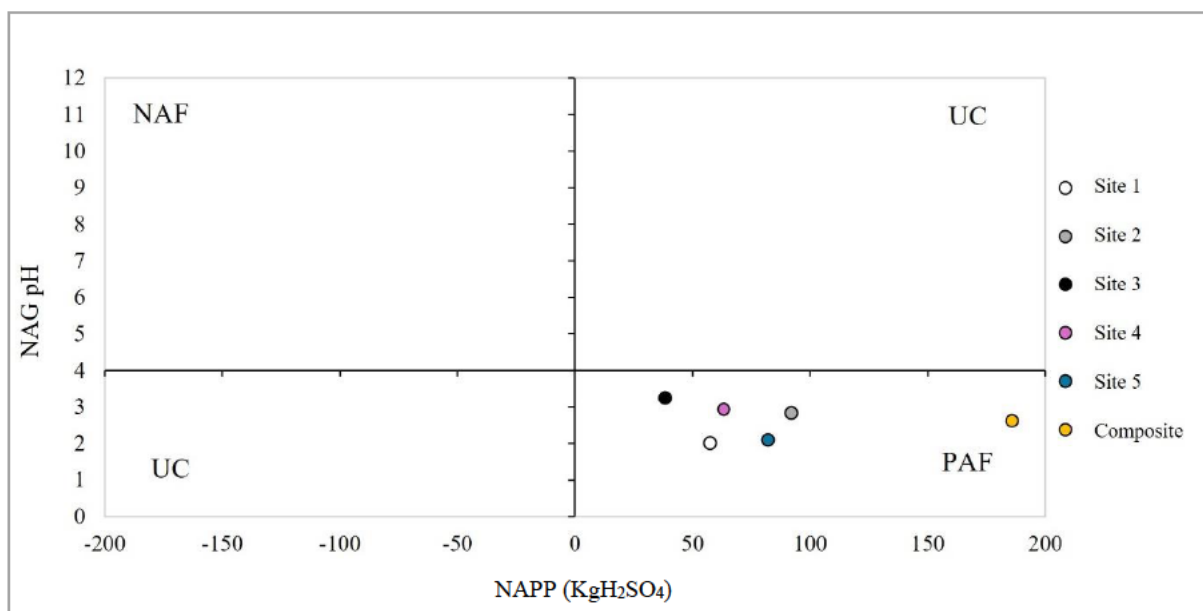


Figure 4: Geochemical classification plot of the IDDS.

ANC/MPA Ratio

This is an alternate way of assessing the acid-base account and risks attributable to the coal mine discarded material. This ratio provides an indication of the relative margin of safety within the material (or lack thereof). Past research indicates that safe values of ANC/MPA range from 1-3 (Smart *et al.*, 2002). A positive (+ve) NAPP is equivalent to an ANC/MPA ratio less than 1, while a negative (-ve) NAPP is equivalent to an ANC/MPA ratio greater than 1 (Smart *et al.*, 2002). All samples yielded ANC/MPA ratios smaller than 1, indicate a potential acid generation risk. The data generated enabled the plotting of an Acid Buffering Characteristic Curve (ABCC) for the composite sample. The ABCC test incorporates the slow titration of a sample with acid whilst continuous pH monitoring and provides an indication of the acid-neutralization potential of the sample.

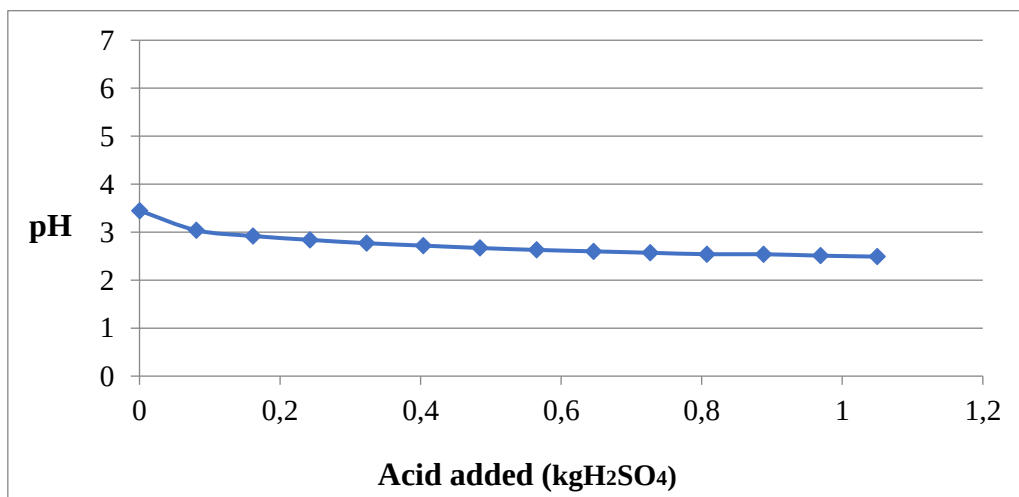


Figure 5. Acid Buffering Characteristic Curve for the Composite Sample.

The ANC (kgH₂SO₄/t) for the composite sample was calculated at 30.35, and results shown in Figure 3 indicate a gradual increase of acidity from pH 3.5 and stabilizing at pH 2.5, indicating that the composite sample does not have enough readily available carbonate to render it non-acid producing. Subsequently indicating high acidity.

Conclusion

The coalfields of the province of KwaZulu-Natal are extensive and have been mined for several decades. Numerous abandoned discarded dumps litter the countryside, many of which are thought to pose potential threats to the natural environment through acid generation. The IDDS, one of the larger discard dumpsites in this area was studied in detail to assess its AMD status. Static testing results indicate significant AMD-generating potential (positive NAPP and PAF for all samples) although the degree of acid production varies for different sites. This is related to various factors including the variability of the material composition of material composing the dump, the minor topographical character of the dump's upper surface that allows pooling of water in specific sites and the spontaneous combustion of parts of the dump that has been occurring for past years. Analysis of the metal composition of the discarded coal indicated the presence of 33 metals, several of which occur in high concentrations and pose a contamination threat, Ba, Sr and Zr with the highest concentrations respectively. Since these metals were not detected in the surrounding surface water resources in a related study, it is presumed that they may be slowly leached to subsurface water where residence times may be lengthy. Rehabilitation of this discarded dump, as well as others in the area, will greatly reduce the risk of environmental deterioration.

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Declaration

There is no conflict of interest among the authors.

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Paper 3:

Kinetic Testing of Acid mine drainage from the Indumeni Discard Dump Site, Klip River Coalfields, KwaZulu-Natal, South Africa.

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ABSTRACT

Acid mine drainage (AMD) results from the oxidation of sulfide bearing minerals on atmospheric exposure and hydration. The resultant sulphuric acid and low pH of the drained water accelerates rock, soil and sediment solubility, enhancing metal and metalloid leaching into and degrading the condition of the natural environment. Assessment of AMD is normally achieved using static or kinetic methods. The former is based on acid-base accounting whilst the latter incorporates the dynamics of the actual AMD generation process by focusing on weathering rates and, leachate ion abundance. In this study, kinetic testing is used to characterise the AMD of the discard material extracted from the Indumeni Discard Dump site (IDDS) located in the Klip River Coalfields of South Africa. Five samples were extracted from the IDDS and subjected to kinetic testing using humidity cells over a period of 22 weeks. A broad range of elements were identified in the leachate of which 11 were used in the analysis. Data from the chemical analysis was used to generate analyte production rates and to assess the acid generation and neutralizing characteristics. The low carbonate production coupled with high sulphate confirms the potentially acid forming character of the discard coal as confirmed by prior static testing.

Key Words: Kinetic testing; leaching; humidity column; weathering rates

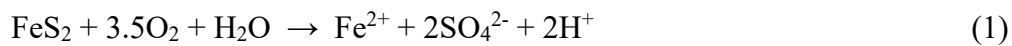
Introduction

South Africa is richly endowed with a wealth of mineral resources having developed an expansive mining industry (Xulu *et al.*, 2021). The country's history of gold and coal mining, in particular, spans over 100 years (Mathu, 2014) and these commodities, together with others, have been important foreign exchange earners (Wang, 2023). Whilst the extensive exploitation of these resources has continued for more than a century, virtually all of the early mining endeavours have operated in a milieu of little to no concern for the natural environment. The adverse mining effects on the environment extend to surface and ground water systems, agriculture, soil and air pollution (due to smelter emissions) and, deterioration of ecosystems (Dehkordi *et al.*, 2024; Adnan *et al.*, 2024). Prior to the promulgation of legislation to control mining activities, mining companies, once mining operations ceased and mines closed down,

simply abandoned operations together with the huge discard dumps that now litter the landscape in mining regions. It is no surprise then that there were 5906 abandoned mines that needed rehabilitation as at end May 2008, creating a major strain on the scarce water resources and endangering vulnerable ecosystems (Auditor General, 2009). Currently, exact figures of abandoned, derelict/ownerless mines are unknown but are likely equally as numerous since little has actually been done due to financial constraints. In South Africa, gold and coal mining, despite being important for revenue generation, have resulted in unwanted environmental consequences (Baloyi *et al.*, 2024). The foremost of these is the production of acid mine drainage (AMD) together with metal enrichment of water resources (Akhtar *et al.*, 2021). This is the fore-runner to despoilation of water resources, soil and habitat destruction with loss of biodiversity. Whilst coal, the focus of this study, may contain a host of different minerals that may lead to acidity, AMD is dominantly caused by the oxidation of the mineral pyrite (FeS₂) (Weber *et al.*, 2006; Tu *et al.*, 2002).

Prior to mining, in their natural, undisturbed state, oxidation of such minerals and the sulphuric acid formation is a function of natural weathering processes. Therefore, the oxidation of undisturbed rock strata and ore bodies followed by release of acid and mobilization of metals is slow and in accordance with the geologic norm. However, extraction and beneficiation operations increase the chemical reaction rates, exposing large volumes of sulphide rock strata to water and air (Kimmel, 1983; Johnson *et al.*, 1987; Kaeser and Sharpe, 2001; Bannerjee, 2014).

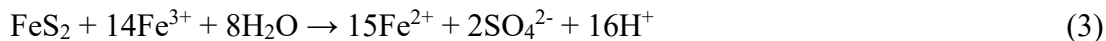
Once pyrite in rock material and coal is exposed to water and oxygen due to mining, it oxidizes to form Fe²⁺, SO₄²⁻ and H⁺ (RoyChowdhury *et al.*, 2015). The overall pyrite oxidation reaction is expressed as follows (Stumm and Morgan, 1981):



The Fe²⁺ ions produced from this reaction interacts with O₂ to form Fe³⁺. This reaction is catalysed by sulfur-oxidizing bacteria, *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* (primarily the latter) which are indigenous to aqueous environments (Kleinmann and Crerar, 1979). The bacteria utilize energy produced from this reaction for their own metabolism (RoyChowdhury *et al.*, 2015):



The Fe^{3+} thus produced further oxidises pyrite to form Fe^{2+} , SO_4^{2-} and H^+ ions:



The abiotic rate of pyrite oxidation by Fe^{3+} is much higher than water and O_2 (Bannerjee 2014). Due to H^+ ion production, the pH drops, and the surrounding environment becomes acidic. If the pH remains in the vicinity of 3.5–4.0, then Fe^{3+} precipitates in the form of $\text{Fe}(\text{OH})_3$. The yellow-orange coloured precipitation of iron hydroxide is known as “yellow boy.”



Due to high acidity, the metal mobility in the environment increases significantly. Extensively acidic pH (as low as 2–4 standard units) coupled with metals toxicity can elicit severe impacts on aquatic biodiversity (RoyChowdhury *et al.*, 2015).

Given the large number of abandoned, un-rehabilitated mines and discard dumps in the area of study, the ongoing AMD generation has already resulted in considerable environmental degradation and requires urgent quantification. This would serve as a precursor to developing and administering ameliorative measures. This study is aimed at achieving this goal through a detailed program of research focused on one of the largest coal mine discard dumps on the Klip River Coalfields, the IDDS. Aspects of the water quality characterization as well as the acid-base accounting of the discard material from the IDDS have been presented in two research papers by the author. Here, the focus is on the kinetic testing of the discard material.

The kinetic methods provide information not obtained in the static acid-base accounting tests. Specifically, information relating to weathering rates and ion abundance from the leachate. Kinetic tests therefore aids in predicting AMD potential in the long term, and attempt to incorporate the dynamics of the chemical, physical and biologic elements, bringing the prediction closer to the reality of the situation (Blowes *et al.*, 2003) Whilst there are several kinetic methods available, this study used the leaching column tests to conduct the kinetic tests on five samples from IDDS.

Study Area and Methods

The study area is the Indumeni Discard Dump Site (IDDS) located in the Klip River Coalfields of South Africa in the northern part of the KwaZulu-Natal Province (Figure 1). This coalfield is the largest of three such coalfields in the province.

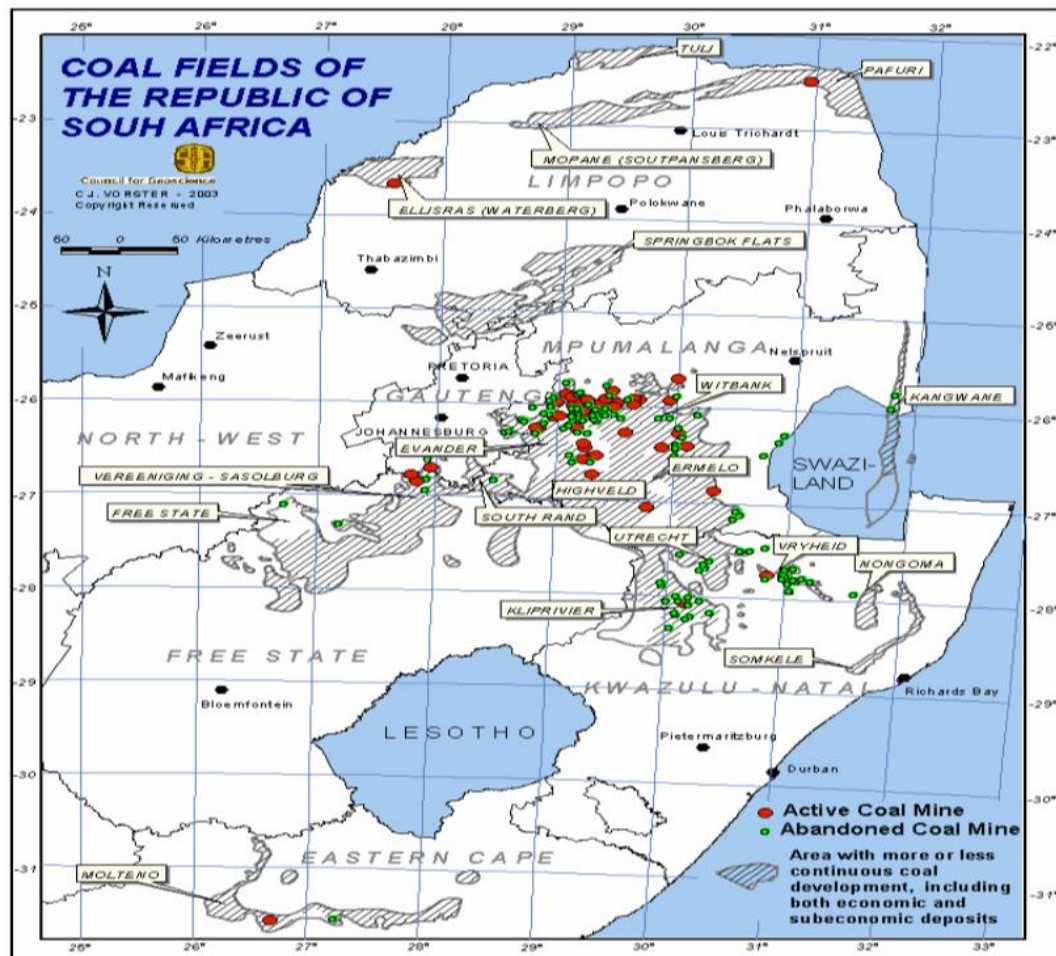


Figure 1: Location of coalfields in the north-eastern portion of South Africa. KwaZulu-Natal Province is located on the eastern seaboard and the Klip River Coalfield located in the northern part of this province.

The area is located within and forms part of the Endumeni Local Municipality (Figure 2) which is one of four local municipalities that comprise the uMzinyathi District Municipality. The Indumeni Local Municipality relatively small (1610km²) and is 290 km north of Durban which

is a major port city and 360 km south-east of the city of Johannesburg (UDM, 2016). There are three towns within this municipality, all of which have well-established road, rail and infrastructure network (UDM, 2016), a legacy of coal mining in the area. The towns are Dundee (a historical battlefield area and now tourist attraction), Glencoe and Wasbank (the latter a small town at the base of the Endumeni Mountain). The uThukela River is a major fluvial system that drains the region whilst the Sandspruit River, a tributary of the uThukela, flows through the study area (UDM, 2016). Specifically, two tributaries of the Sandspruit River drain the area in the vicinity of the IDDS: the Biggarsgatspruit River which flows in close proximity to the IDDS on its eastern side and, the Wasbank River (Figure 2).

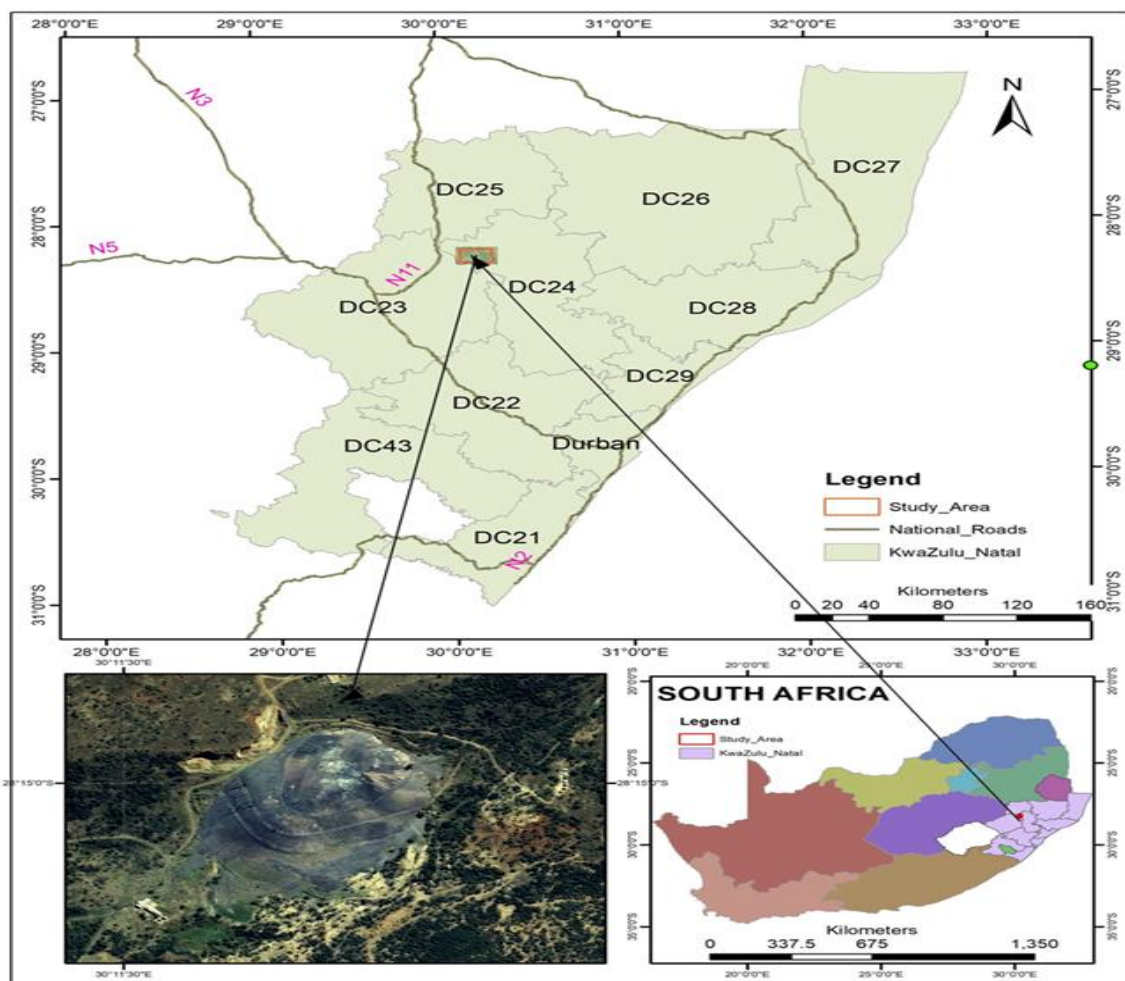


Figure 2: Location of the Indumeni Discard Dump Site within the uMzinyathi District Municipality (DC24 on the map), within the KwaZulu-Natal Province of South Africa.

(Adopted from Govender S, 2025 submitted for publication).

The discard dump is located at 28° 15' 16.7" S and 30° 11' 33.0" E, approximately 12 km to the SW of the town of Dundee. Although the dumpsite is situated on a slope, the site had been excavated to create a relatively flat platform prior to dumping. Consequently, immediately above the north side of the dump, the slope elevation is 1200m amsl whilst the slope elevation on its south side is 1160m amsl. At the time of sampling, the IDDS covered an area of approximately 11Ha at its base with an upper surface area of approximately 3.5Ha due to tapering of the slopes of the discard material. Maximum elevation of the dump was approximately 19m from its base. According to DWS calculations, the volume of material contained amounted to over 1 506 507 m³ with an estimated mass of 1 657 157.7 metric tons. A considerable portion of the discard material is made up of moderate to low-grade coal, hence there have been several instances of spontaneous combustion at different parts of dump over the years. These spontaneous combustion events have mainly been restricted to the surface layer of the discard material, to depths of no more than a meter. Since 2017 secondary mining of dumpsite commenced and this has continued to date. Whilst the secondary mining will remove large quantities of the discard material, a considerable amount is anticipated to remain as not all of the material would have sufficient economic value.

Geology of Study Area

The geology of the study site part of the Vryheid formation (Ecca Group), (Catuneanu *et al.*, 2005). The sedimentary rocks that form part of Vryheid Formation represents some of the most distal facies of the Ecca interior seaway (Green *et al.*, 2012). This was deposited during gradual transformation from marine to non-marine conditions leading to the formation of extensive coal deposits within a mudstone–sandstone succession (Green *et al.*, 2012). The coal is categorized as bituminous and anthracite coal and characterised by elevated concentration of phosphorous and sulphur (Jeffery *et al.*, 2015).

Climate

The climatic condition of the Wasbank area is classified as Cwb according to the new Köppen Greiger classification system to quantify climatic conditions. The climatic conditions characterised are hot summers, dry winters and a warm temperate climate. Annual mean minimum temperatures range from 10.1°C and 16.7°C and 21.6°C and 23.9°C and annual mean

maximum temperatures range from 24.2°C to 27.4°C to 40.1°C and 42.4°C respectively (SAWSA, 2020). Mean annual precipitation ranges from 550 millimetres (drier and low-lying regions) to 2000 millimetres with most rainfall occurring from October to January (Worlddata.info, 2021).

Topography

The district is characterised by extensive variation with deep river gorges, grasslands, extensive wetlands, hills and valley bush-veld (UMDM, 2019) with a maximum altitude of 3443 meters (Topographic-map.com. The town of Wasbank (within the study area) is located at 1069 meters above sea level (masl) (FloodMap.net, 2021) and the discard dump location is within the north-eastern part of the town with an undulate mountainous terrain.

Land use

The major economic sector within this municipality includes social services (2.16%); trade (13.64%); private household/domestic workers (13.49%); farming (9.57%); manufacturing (7.39%); business services (4.93%); construction (4.5%); transport (4.48%); mining (1.47%); and utilities (1.03%) (UDM, 2016). Commercial agriculture, plantation and sugar cane farming are the main activities within this district (UMDM, 2019) however, the study area includes an abandoned mine and is dominated by livestock farming. The dominant vegetation type is the Income Sandy Grassland which occupies much of the eastern half of the study area with some extensions to the west in the central part of the study area (Luckan, pers. comm., 2024).

Field Sampling

Due to the undulating nature of the surface of the discard dump, and the marked drop-off slope to the southeast, sampling sites could not be established uniformly equidistant from each other. Also, since there was considerable amounts of ash over portions of the dump, samples were taken at depths where the coal sample appeared unaffected by combustion. Samples of discard coal was collected from five sampling sites located on the IDDS (Figure 3).

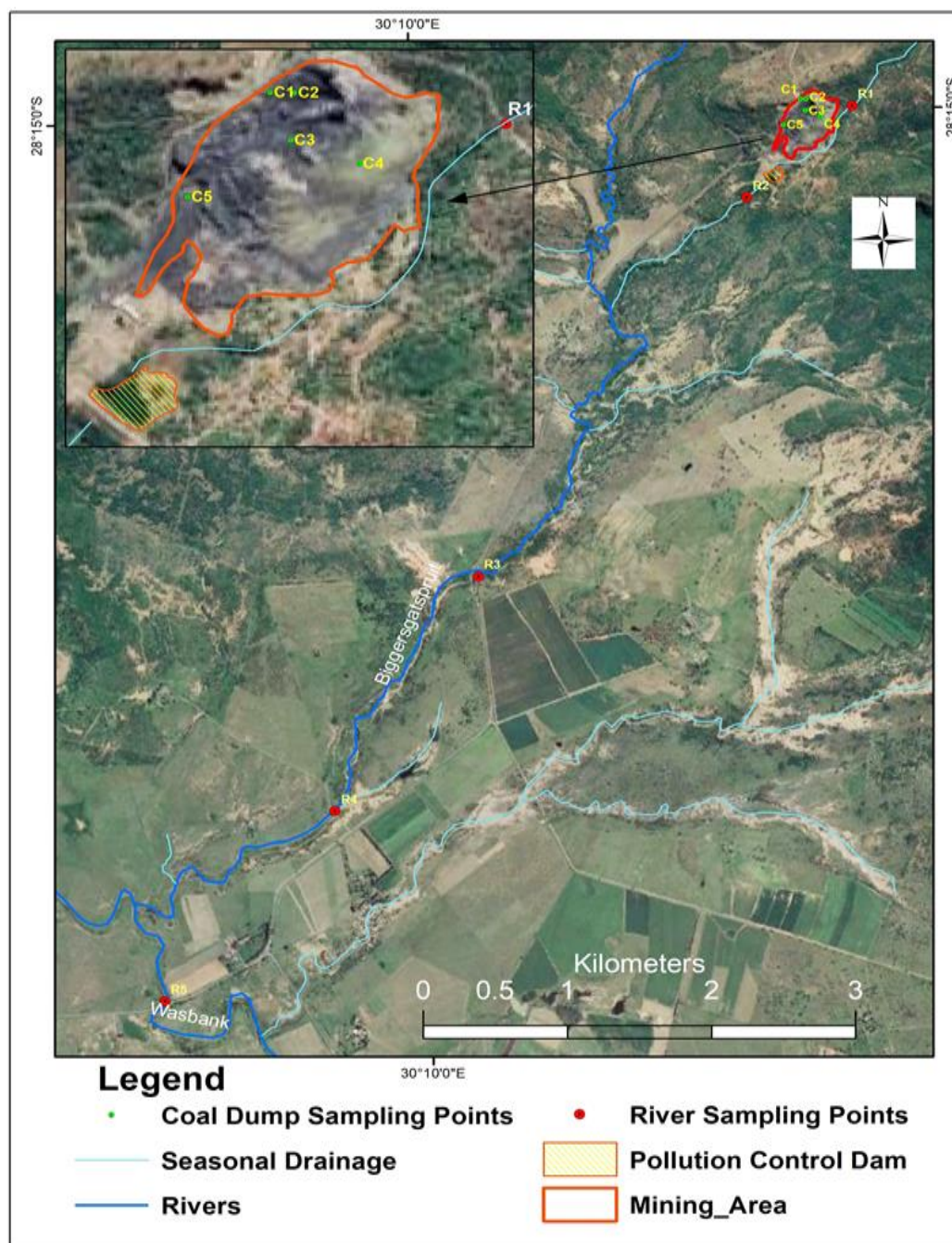


Figure 3: Location of the Indumeni Discard Dump Site (IDDS) and adjacent rivers.
 (Adopted from Govender S, 2025 submitted for publication).

Samples of the discard coal were extracted using a Dutch soil auger and a spade and, both the samples and their sites of extraction were logged. Approximately 2.5Kg each of discard material was taken from each of the five sites and transferred to the laboratory for analyses.

Kinetic Testing

Kinetic testing is a laboratory weathering procedure that involves a series of measurements over a specified time (generally 15 to 40 weeks) to assess a range of acid mine drainage constituents (American Society for Testing and Materials, 2009). The test procedure is used to determine the acidic, alkaline, or neutral drainage of the sample; identify solutes in the effluent; the mass of solutes released; and the rate at which solutes are released (ASTM, 2009). In general, static methods consider the acid-base balance and is widely known in the literature as acid-base accounting or ABA (Sobek *et al.*, 1978). Kinetic methods, on the other hand, can provide information on rates of weathering and ion abundance in the leachate, which is not obtained in static tests (Bradham & Caruccio, 1999). For instance, following comprehensive laboratory and field tests, Morin and Hutt, (1997) have shown that a greater quantity of mineral reaction dissolution products are released consistently per unit time and per unit weight in laboratory weathering tests. This is because, besides long-term prediction of acid drainage potential, kinetic tests attempt to include biological elements, chemical and physical dynamics, bringing the prediction closer to the reality of the mine (Bannerjee, 2014). Bradham and Caruccio, (1999) point out that kinetic tests provide empirical data by simulating weathering conditions on overburden samples, which can be adjusted to either accelerate or mimic natural conditions. Pyrite oxidation rates and the release of weathering products can be quantitatively measured for drainage quality prediction. The kinetic tests resulting leachates are analysed for parameters such as pH, acidity, alkalinity, sulphate, specific conductance and other constituents (Bannerjee, 2014). This data can then be statistically analysed to evaluate sulphide oxidation rates and acid production.

Whilst the actual details of kinetic tests vary, all are essentially geared toward mimicking natural wetting and drying cycles and, the leaching or flushing of ‘wastes’ (Parbhakar-Fox and Lottermaser, 2015). For this reason, they are usually run over lengthy periods. Sapsford *et al.* (2008) list the most common kinetic tests as Laboratory based columns, humidity cells,

Soxhlet, BCRC and shake-flask/batch reactor tests. The latter two examine the impacts of mine waster bacteria on the formation of acidity (Sapsford *et al.*, 2008; Sobek *et al.*, 1982; Bradham and Carrucio, 1999; Price, 2009).

For this research focus was placed on the leachate chemistry on the laboratory weathering of IDDS discard material with the use and operation of humidity cells to produce acidic, alkaline and or neutral drainage. This method was adopted by the American Society for Testing and Materials, ASTM International, issued under the fixed designation D5744-07. Two protocol options (A and B) comprise the test procedure, differing only in the way oxygen is supplied to the humidity cells. As per the ASTM, (2009) Standard Test Method document, Option A uses weekly cycles composed of three days of dry air (<10% relative humidity) and three days of water saturated air (95% relative humidity) pumped into the sample. This is followed by a leach on day seven. With option B, each cell is stored under conditions of relatively constant temperature and humidity with oxygen supplied by diffusion of ambient air.

For this study, Option B protocol was selected, and five humidity cells (Figure 4) were used in this research that involved the following procedure as stipulated in ASTM (2009):

- Coal discard materials collected per sampling site were crushed to pass through a 6.3mm screen;
- 1000 grams (crushed material) was placed into each humidity cell and filled with one litre (1L) distilled water, i.e., a 1:1 ratio was applied;
- The humidity cells were stored over six days in the laboratory subject to relatively constant conditions of oxygen, humidity, and temperature by diffusion of ambient air, in an environmentally controlled enclosure and,

- Weekly leachates were collected and chemically analysed over a test duration of 22 weeks.



Figure 4: Humidity leach columns for the kinetic testing with weekly leachate.

Discard material elemental classification

These analyses were conducted at the Central Analytical Facilities (CAF), Stellenbosch University, South Africa as follows:

Elemental Content of Waste Rock: X-Ray Fluorescence spectrometry (XRF)

XRF was utilised to identify geochemical concentrations of majors and trace elements for the coal discard. A PAN analytical Axios Wavelength Dispersive spectrometer was used for analysis. The spectrometer was fitted with a Rh tube and the following analysing crystals: LIF200, LIF220, PE 002, Ge 111 and PX1. A gas-flow proportional counter and a scintillation detector was also fitted (CAF, 2021). The gas-flow proportional counter uses a 90% Argon-10% methane gas mixture. The control standards used in procedural calibration for major element analyses fit the range of concentration of the samples. Among the standards were BE-N (Basalt from the International Working Group) and NIM-G (Granite from the Council for Mineral Technology, South Africa) (CAF, 2021). Major elements were analysed with a 2.4kW Rhodium tube. Correction for the matrix effects in the samples was done by applying

theoretical alpha factors and measured line overlap factors to the raw intensities measured with the Super Q PAN analytical software (CAF, 2021).

Leachate analysis

Leachate samples were filtered with a 0.45 micro filter into 100ml bottles. The pH was measured by way of a Microprocessor pH meter and electrical conductivity (EC) was measured with the Inolab Con Level 1 Multiparameter Meter. Both parameters were measured in triplicate. The sulphate analysis was conducted using the ion chromatography. This method analyses anions and cations. This globally accepted method is an alternative to current wet methods for wastewater analysis (Michalski, 2018). The procedure used by the CAF for samples of this study followed the guidelines from Eggins (2003).

The sulphur and carbon analyses were conducted using the Carbon Hydrogen Nitrogen Sulphur (CHNS), Elemental analyser. A portion of the coal discard sample (dry and pulverized) was placed into a combustion chamber and the percentage of hydrogen, carbon, sulphur and nitrogen was obtained. For this research, the percentages of carbon and sulphur were used.

Heavy metal analysis was conducted using a Perkin Elmer 8300 DV Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). This spectroscopic technique is based on photon emission from ions and atoms that have been excited in a radiofrequency (RF) discharge (Helaluddin *et al.*, 2016). This highly sensitive technique has immense advantages in the determination of heavy metals (Chand and Prasad, 2013). Leachate samples were filtered using a 0.45 micro filter into 15ml ICP vials. The samples were acidified with nitric acid (HNO₃). The heavy metals analysed using ICP-OES was Aluminium (Al); Calcium (Ca); Cadmium (Cd); Copper (Cu) Cobalt (Co); Chromium (Cr); Iron (Fe); Lead (Pb); Mercury (Hg); Nickel (Ni) and Zinc (Zn). A range of multi element standards was used to prepare calibration data for sample heavy metal quantification.

Flame Photometry was used to determine the concentration for Sodium and Potassium from the leachate collected.

The results emanating from the analysis were also compared to the 'South African Water Guidelines Target Water Quality Ranges (TWQR)' from the Department of Water and Sanitation (DWS, 1996) for domestic, industrial, and aquatic ecosystems.

Results and Discussion

Leachate characteristics

The kinetic leach tests were carried out for five samples (five columns) over a period of 22 weeks and analyses were made for pH, EC, Na, K, Al, Ca, Cu, Fe, Hg, Ni, Pb, SO₄ and Cl.

The mean pH is indicative of the general acid nature of the leachates. Na, K, Cu, Ni, Zn and Cl are largely within the acceptable mean concentration range, however the other analytes show great variability, often in concentrations that are toxic.

The key advantage of kinetic testing is the ability to demonstrate weathering rates and elemental loading of the leachates. The reaction rates of the analytes were plotted as a function of time to aid prediction of amount of alkalinity or acidity produced. Bannerjee (2014) and others have asserted that carbonate dissolution and pyrite oxidation are important because this aids identification of which suite of species weathers faster – the acid producers (sulphides) or the neutralizers (carbonates).

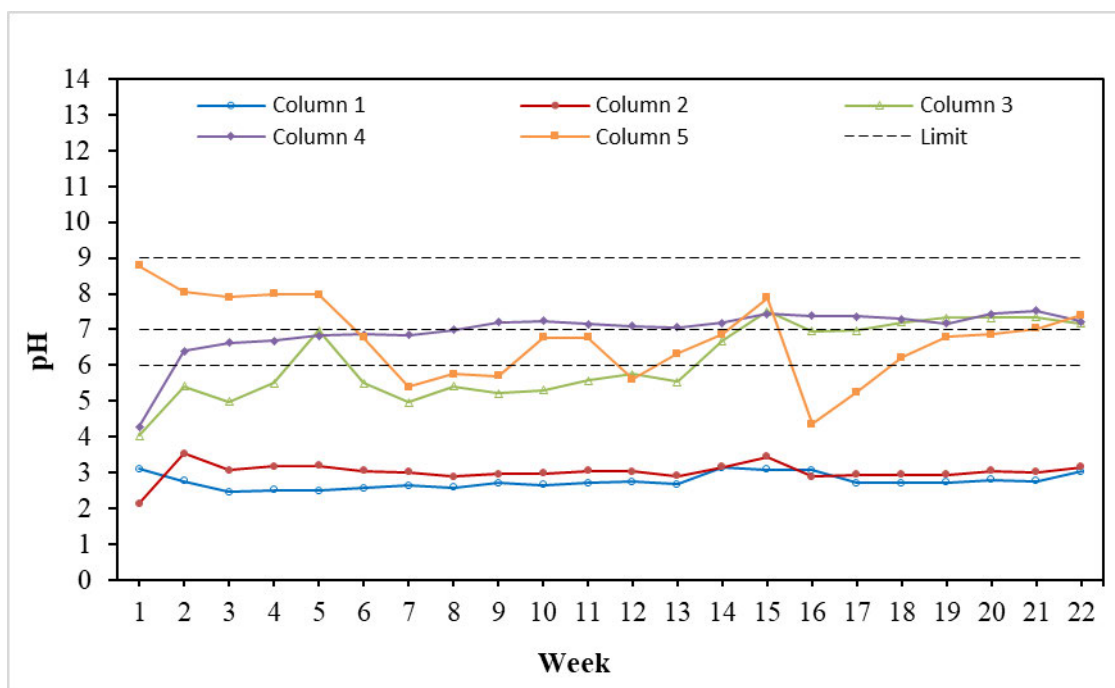


Figure 5: pH of the leachate for the five columns for the leaching period.

The leachate pH for the five columns is shown in Figure 5 and represents 110 analyses of pH (excluding those carried out during the initial flushing phase). The mean pH (5.12) is below the acceptable standard and confirms the general acidic nature of the leachates. Column 4 was consistently in the near neutral pH except at inception when there was a rapid improvement from pH 4 to neutral. Column 5 leachate was, for distinct periods, within the acceptable pH range with very noticeable weekly fluctuations. pH for this column dipped below 6 for three periods: weeks 6 to 9, followed by week 12 and then weeks 15 to 18. These results indicate rapid changes in acidity and neutralization of this column material with time. Column 3 also yielded similar results to Column 5 except that it commenced from acidic to neutral whereas Column 5 presented the opposite scenario. Column 1 and Column 2 presented consistently acidic leachate (approximately pH 3 over the entire leaching period). Samples for these two columns come from the upper portion of the discard dump where the material appeared to be relatively free from traces of prior instantaneous combustion. The final pH following the 22-week testing period was almost neutral for Columns 3, 4 and 5. For Columns 1 and 2 the final pH was still approximately 3.

The sulphate concentration of Column 1 ranged from 1888.43mg/l to zero in five of the measurement weeks, with a mean concentration of 958.50mg/l. Ca concentrations remained relatively low with some high concentrations measured. The mean Ca concentrations are of the order of 123.07mg/l and points to relatively strong neutralizing capacity.

The concentrations of analytes were assessed for their relative levels of toxicity using the South African water quality target ranges (TWQR) for aquatic (A), domestic (D) or agricultural use (AG). With the exception of Ca concentrations of the Column 1 leachate, all Columns yielded several weeks of very high Ca concentrations, exceeding even the TWQR for domestic water use ($< 32\text{mg/l}$) for several of the weeks of testing. This is also shown in the mean Ca concentration (all columns) of 123.07mg/l.

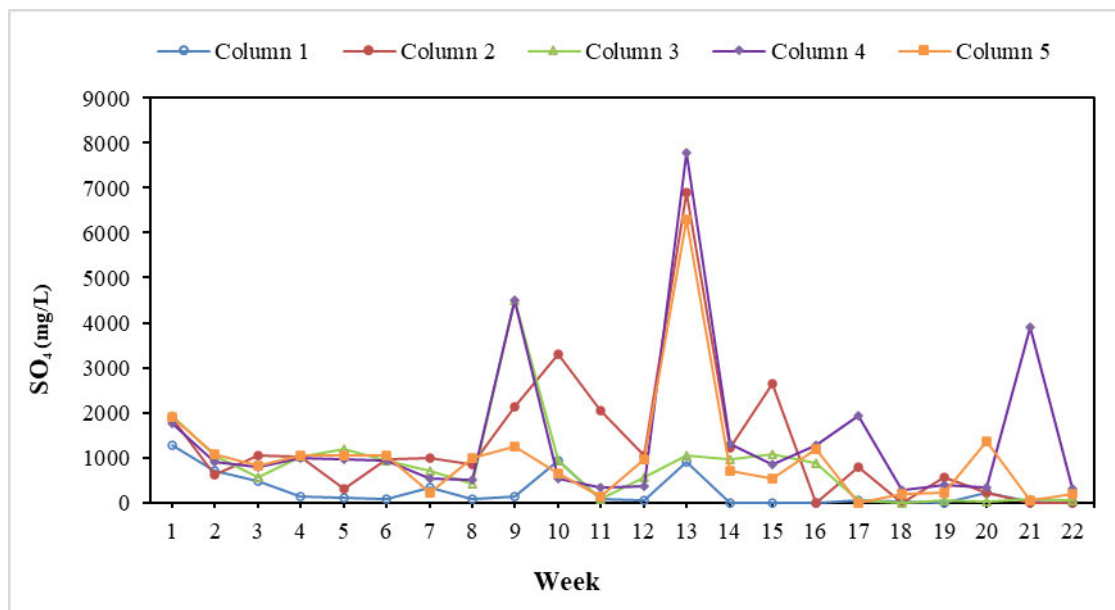


Figure 6: Sulphate production over the 22 weeks of testing.

Sulphate production trend showed a gradual decline until week 8 when production began to fluctuate for all columns. Columns 3 and 4 displayed the first spike to identical concentrations of 4493mg/l in week 9. The first spike for columns 1 and 2 occurred in week 10 with sulphate reaching 928.2mg/l and 3294.9mg/l respectively. A dramatic spike in sulphates occurred in week 13 for column 2 (6889.2mg/l), column 4 (7787.8mg/l) and Column 5 (6290.2mg/l). Column 3 yielded a sulphate concentration of 3893.9mg/l in the penultimate week of testing. With the exception of column 1, all columns showed the production of very high sulphates, ranging from 7787.8mg/l to the very few weeks when no sulphates were detected. Overall, mean sulphate concentrations far exceeded those stipulated in the ‘South African Water Quality Standards’ and are in keeping with the static testing results that showed all samples as potentially acid forming (PAF). The TWQR for domestic use of water is 0 – 200mg/l and this value was exceeded for 79 of the total 110 weeks of testing.

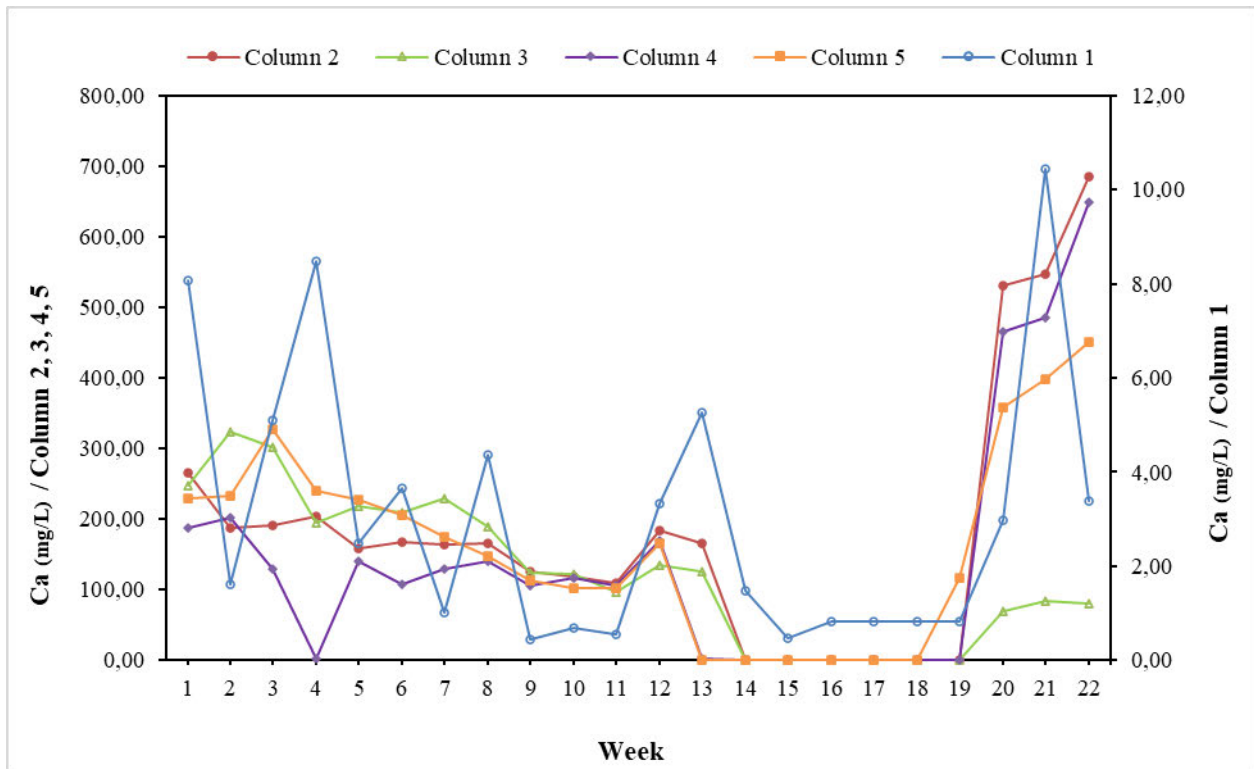


Figure 7: Ca production from Column 1(scale on the right) and Columns 2 – 5 (scale on the left).

Calcium concentrations in the leachate matrix demonstrated a rather unique and consistent pattern for Columns 2 to 5. The period from week 14 to 19 showed a sharp decrease in concentrations to $< 1\text{mg/l}$ for the most part. Except for week 4 of Column 4, when Ca production was 1.46mg/l , the Ca production of Columns 2 – 5 recorded high Ca concentrations from inception up to week 14. The sudden and consistent low Ca for weeks 14 to 19 for all samples most likely reflect consistency in the mineralogy of the samples. There is a rapid spike in Ca production for the final 3 weeks of testing.

The Ca production is indicative of a moderate neutralizing capacity due to the rapid weathering. But the rapid weathering will also result in rapid exhaustion of the neutralizing capacity with the potential for long term acidity to resume.

The production rate of Fe showed a rapid drop from a high of approximately 0.85mg/l to zero. Fe concentrations were therefore low for all columns ($< 2\text{mg/l}$).

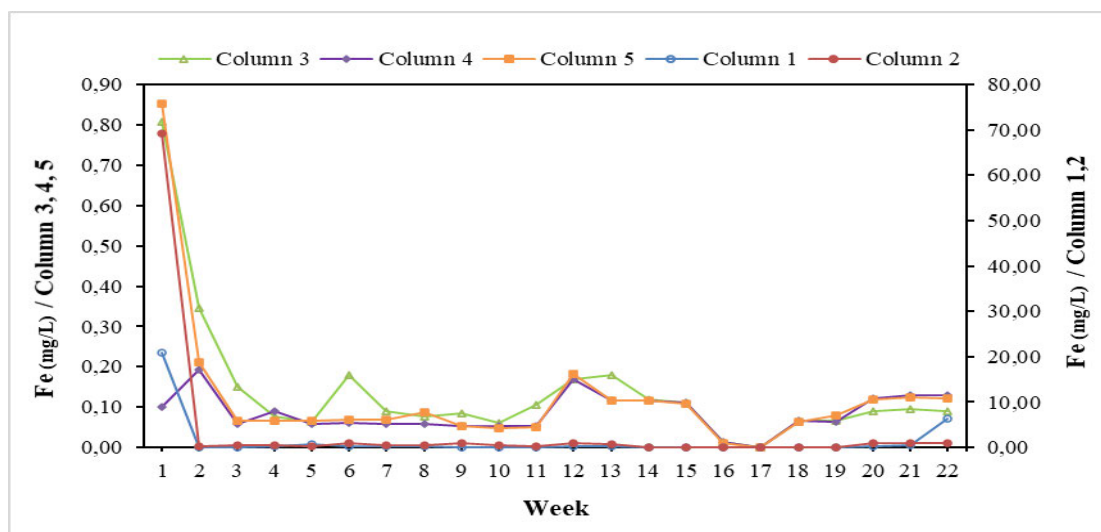


Figure 8: Fe production for Columns 1 and 2 (scale on the right) and Columns 2. 3. 4 and 5 (scale on the left).

With regards to Fe, concentrations were within the TWQR (AG: 0-10mg/l) but did exceed the domestic standards ($< 0.1\text{mg/l}$) for Column 1 (13 weeks) and Column 2 (19 weeks). Overall mean Fe concentrations (1.01mg/l) would render the water unfit for domestic use.

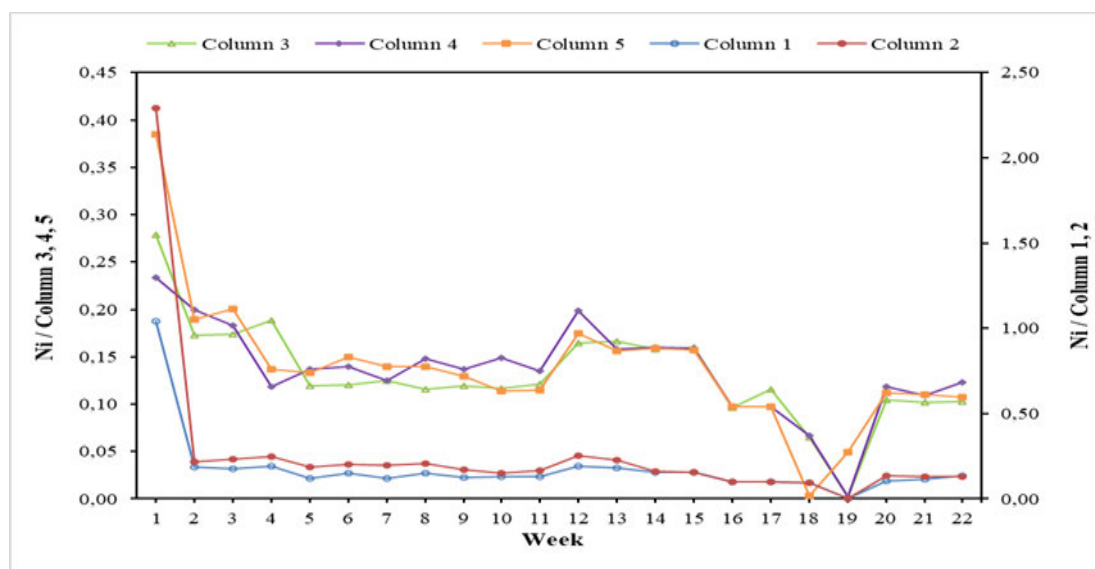


Figure 9: Ni production for Columns 1 and 2 (scaled on the right) and Columns 3 – 5 (scaled on the left).

The TWQR for Ni (AG) is 0 – 2 mg/l. Ni production for all columns were below the upper limit of the TWQR for Ni and therefore of no concern (Figure 9). However, Pb production

(TWQR = 0.001 – 0.2) (Figure 10) was high for all Columns and all weeks except the period week 14 to 19. The mean Pb production was 0.76mg/l which exceeds the upper TWQR (A). The total Ni production was 15.13mg/l with a mean of 3.03mg/l whilst the total Pb production was 36.16mg/l with a mean of 7.23mg/l. This implies that should Ni derived from the leaching of the discard dump be concentrated in the environment, it will easily reach toxic levels.

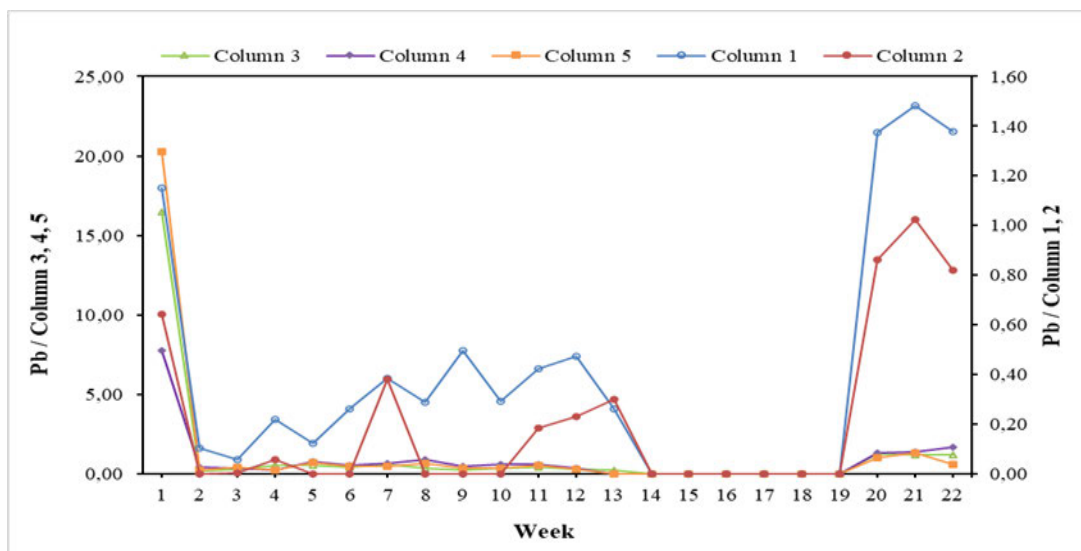


Figure 10: Pb production for the 22 weeks. Columns 1 and 2 scaled on the right) and Columns 3 – 5 scaled on the right).

Relatively higher Al was produced at Columns 1 and 2 (4.93mg/l total and 97.87mg/l respectively). These levels exceed both the aquatic and agricultural TWQR for Al (< 5mg/l) and are therefore likely to create negative impacts to the natural environment. In similar vein, Al displayed a similar trend to Ni and Pb in demonstrating a fall-off in production rates for the weeks 14 to 19.

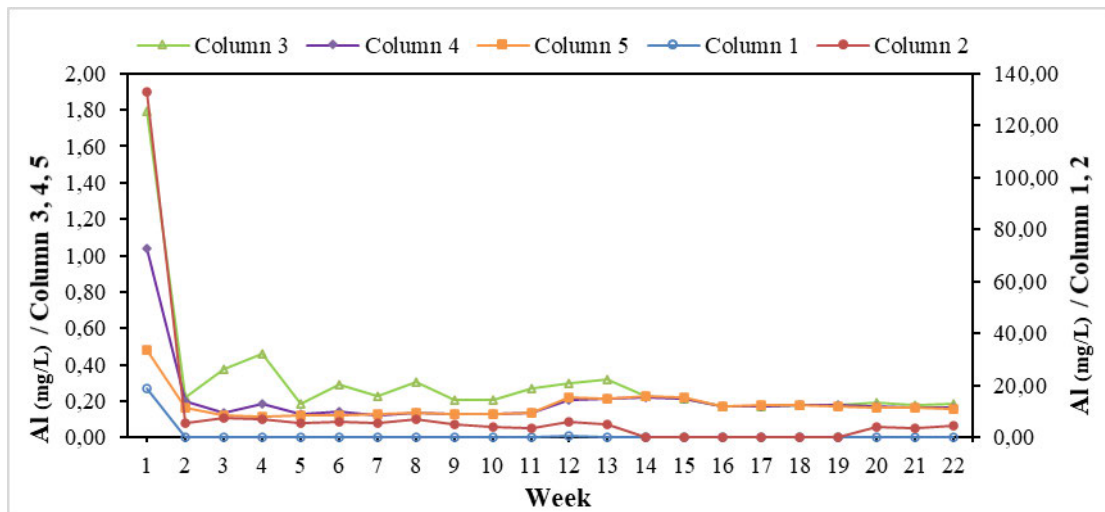


Figure 11: Al production for the 22 weeks. Columns 1 and 2 scaled on the right) and Columns 3 – 5 scaled on the right).

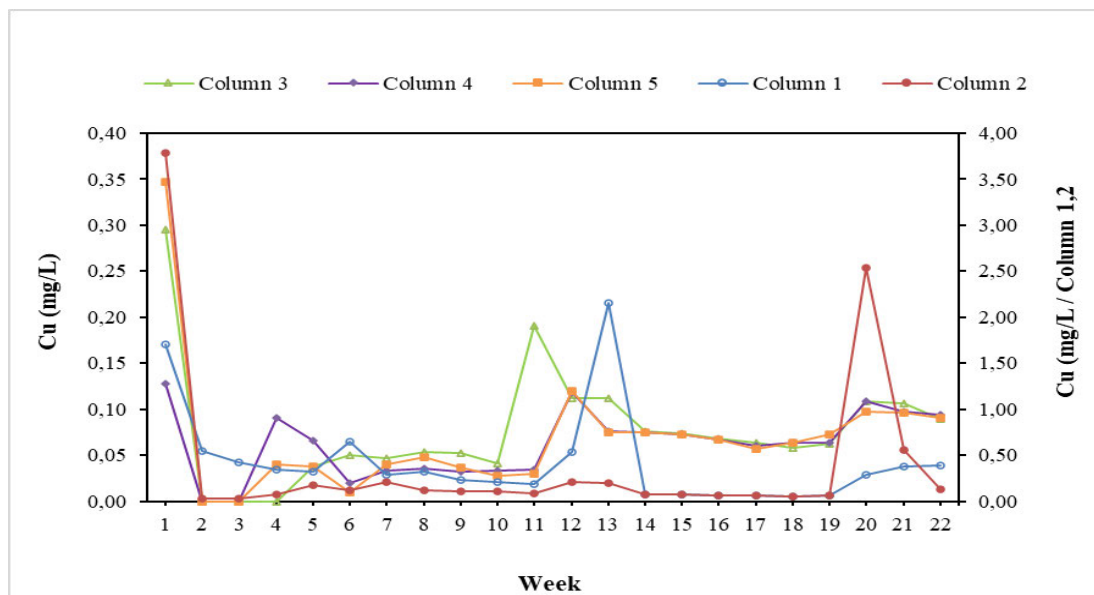


Figure 12: Cu production for the 22 weeks. Columns 1 and 2 scaled on the right) and Columns 3 – 5 scaled on the right).

Cu production showed a rapid initial drop in concentration from week 1 to weeks two and three and thereafter yielded low concentration output throughout the leaching tests. A slight anomaly is seen at week 11 for Column 3 when concentration reached 0.19mg/l , week 13 for Column 1 (2.15mg/l) and week 20 for Column 2 (2.54mg/l). These three values exceeded the TWQR

(D) which is $[\text{Cu}] < 2\text{mg/l}$. The decrease in production from week 14 to 19 is evident for Cu as well.

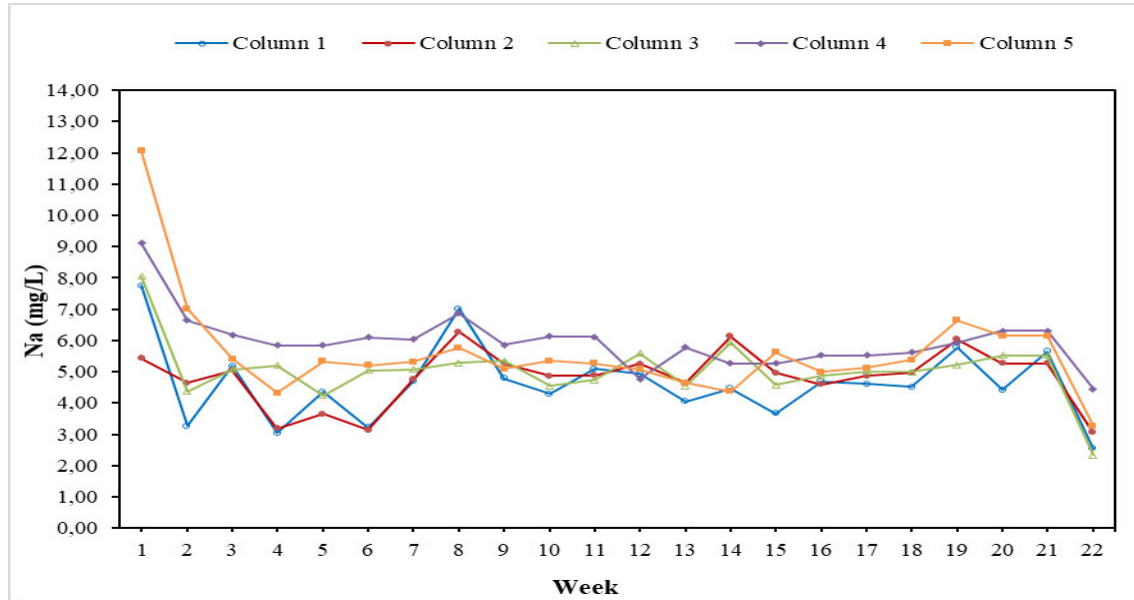


Figure 13: Na production for the 22 weeks.

The release of Na was fairly consistent at 3 to 7mg/l for all five columns and throughout the testing period. Within this band of Na release, fluctuations have occurred. The relatively constant release of Na is directly related to state in which Na occurs in coal. According to Wang *et al.*, (2024), Na is present in coal in a water-soluble state, largely (>70%) in a hydrated state as $\text{H}_2\text{O-Na}$. This implies that minerals randomly distributed within the coal are not the primary sources of Na. Instead, the Na, when present, is fairly homogenously distributed within the coal seam. Hence, weathering will release Na in a relatively constant concentration over time.

A consistently low concentration of K, with minor fluctuations, characterized the entire leaching test result for all five columns (Figure 14). Since K is known to occur in the clay mineral illite (Spiro, *et al*, 1986), its release will be related to the presence of illite in each of the columns. The minor spikes shown in the production curves for K are indicative of the weathering of these specks of clay minerals in the samples. In terms of the TWQR for K in the leachate, all columns yielded K in concentrations significantly lower than the domestic standard of <50mg/l.

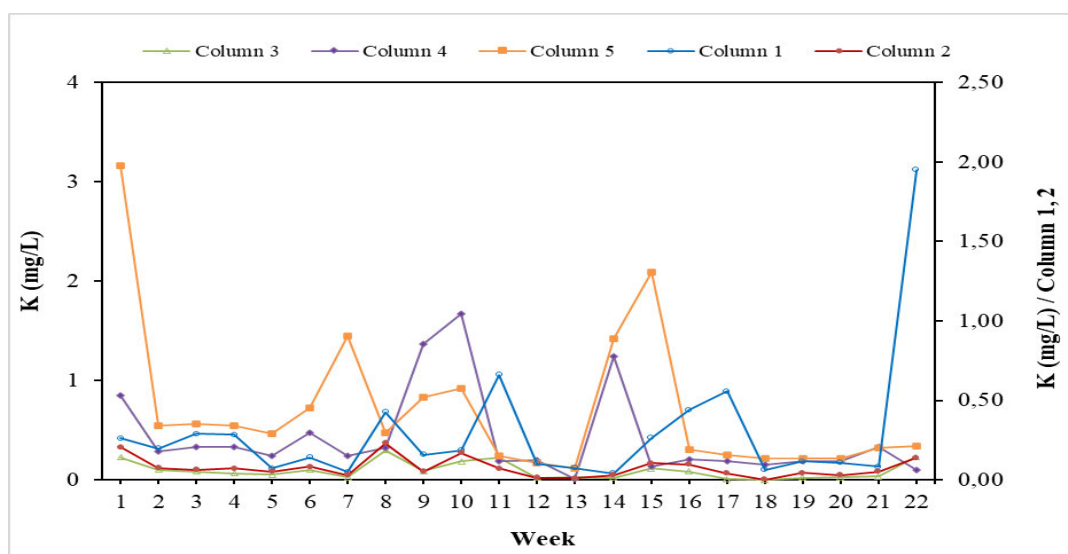


Figure 14: K production for the 22 weeks. (Columns 1 and 2 scaled on the right and Columns 3 – 5 scaled on the right).

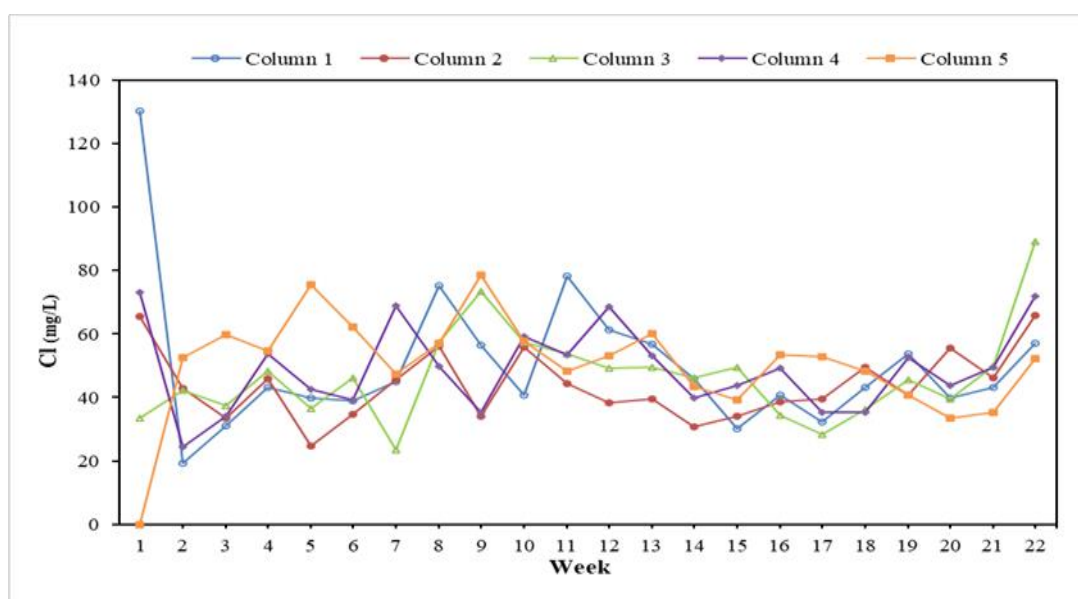


Figure 15: Cl production for the 22 weeks for all five columns.

The production of Cl for all columns ranged between 20 and 120mg/l with regular fluctuations from week to week (Figure 15). This amount of Cl production is far below the domestic TWQR of <200mg/l and is therefore not a potentially serious source of contamination following long term weathering of the coal. Contamination may however still occur through concentration in water bodies.

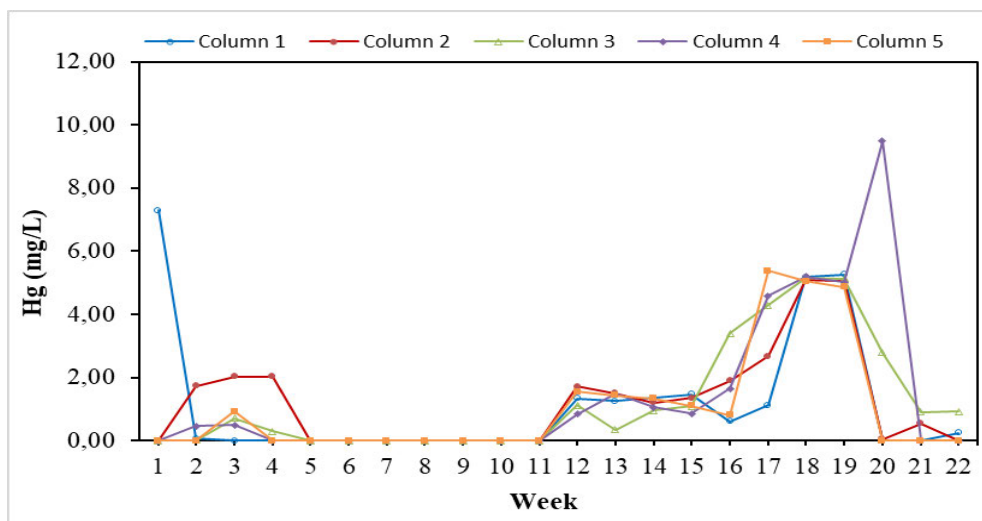


Figure 16: Hg production for the 22 weeks for all five columns.

The production of Hg (Figure 16) followed a unique path, different from the other analytes. Initially, there was some production of Hg, presumably through the dissolution of the mineral Galena. Thereafter, for a lengthy period of six weeks, there was minimal production of HG (<0,7mg/l) from Column 5 and none from the other columns. Thereafter, production resumed from all columns, as more Hg bearing minerals became exposed to the weathering front, reaching a peak concentration of just over 5mg/l for all columns before decreasing towards the end of the leach period. The only exception is Column 4 where the highest concentration of 9.48mg/l was recorded. With reference to the water quality standards, this production of Hg is of concern. The domestic standard requires Hg concentrations to be below 0.000001mg/l and the concentrations yielded from the leach test showed that, when present, Hg had reached toxic levels.

The EC curves (Figure 17) indicate an initial rapid drop off for the first two weeks to approximately 200mS/m for columns 2 – 5 followed by a very gradual decline to approximately 150mS/m. this pattern is expected given the gradual overall decline in production of analytes over the leach test period. The exception is Column 1 where EC levels were very low throughout.

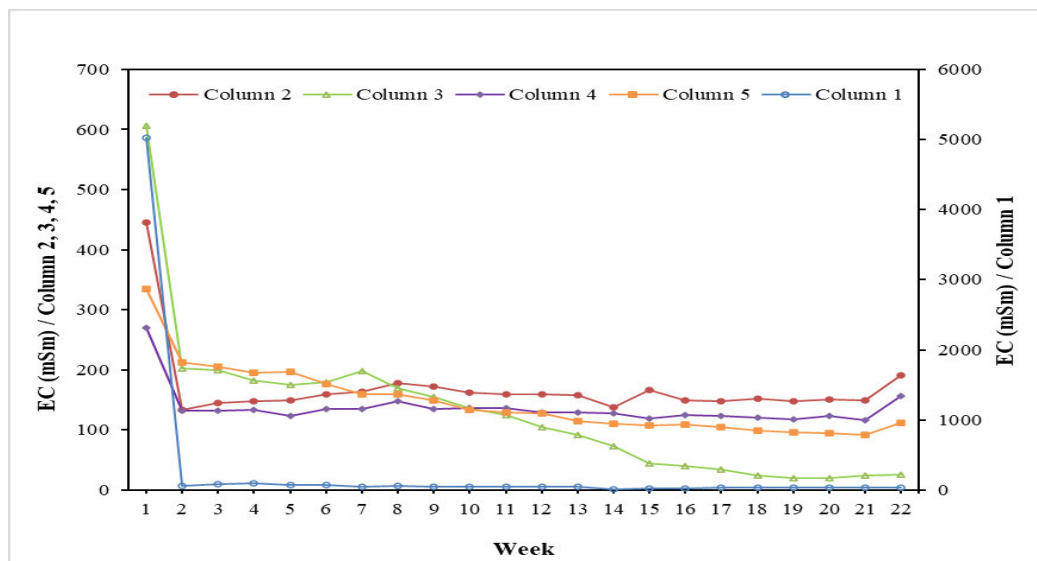


Figure 17: EC measurements for the leachate for the 22 weeks. Column 1 scaled on the right) and Columns 2 – 5 scaled on the right).

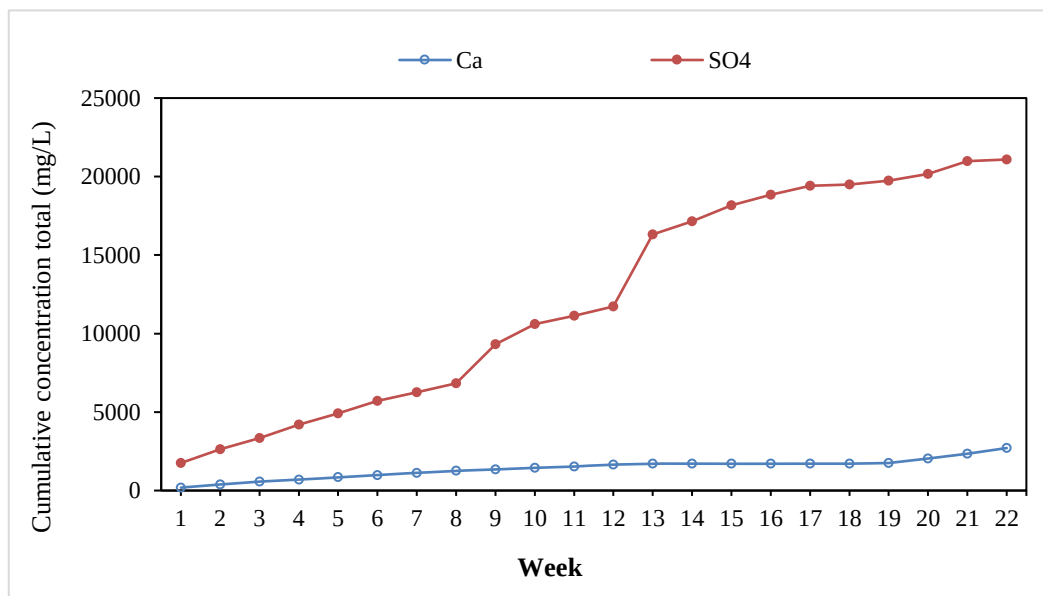


Figure 18: The cumulative Ca (carbonate) and SO₄ production over the 22-week period.

Figure 18 above shows the cumulative sulphate and carbonate (as Ca) weathering rates. Comparison of the two curves shows the relative production rates and which of them will likely be exhausted first. Clearly, the rate of sulphate production far exceeds that of carbonates, demonstrating the low neutralizing capacity that prevails.

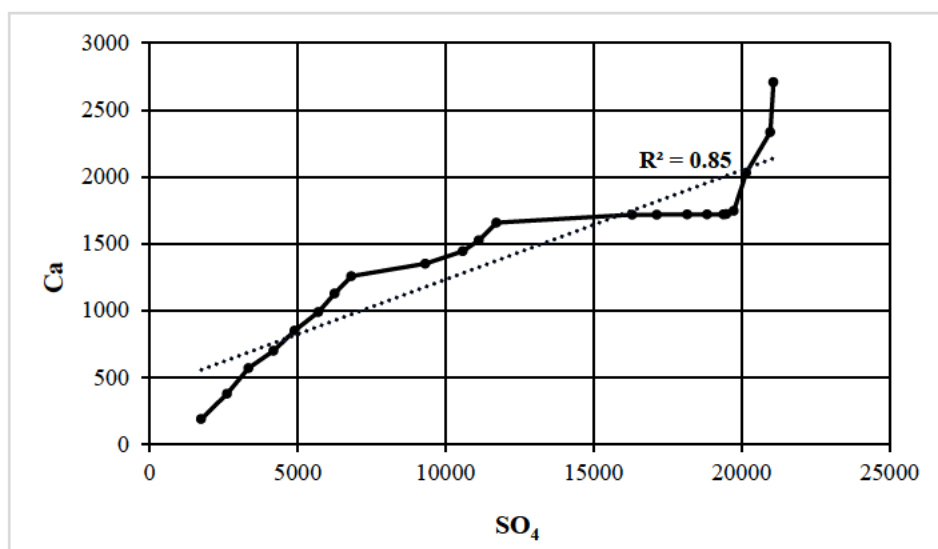


Figure 19: The cumulative mass relationship of sulphates and Ca (carbonate equivalent)

Figure 19 represents the cumulative mass of sulphates (oxidation product) plotted against cumulative Ca (neutralization product). This oxidation-neutralization curve graphically depicts the oxidation – neutralization potentials over the period of the kinetic testing (Mendez-Ortiz *et al.*, 2007; Bannerjee, 2014). The best fit ($R^2 = 0.85$) relation between the acidification and neutralization products indicates that the oxidizing capacity exceeds neutralizing capacity by a ratio of up to 10:1. This ratio may well be an overestimate as not all neutralizing agents were tested. However, static testing on the same samples did confirm the potentially acid forming character of all five samples used in this series of kinetic tests.

XRF Analysis and other mineralogical sources

The sample material used in the kinetic tests were further analysed for their chemical and crystallographic phases as well as crystallinity determination using X-ray diffraction. Samples used in Columns 2, 4, and 5 were found to contain quartz, kaolinite/dickite, illite/muscovite and gypsum while both Column 1 and 3 samples quartz, kaolinite/dickite and gypsum.

Quartz composition is SiO_2 and Gypsum is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Both Kaolinite and Dickite are clay minerals with the same chemical formula $(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4)$. The clay mineral Illite has a fairly complex composition, $(\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}[(\text{OH})_2(\text{H}_2\text{O})]$, whilst the mica, Muscovite is similarly complex: $[\text{KAl}_2(\text{AlSi}_3\text{O}_{10}(\text{FOH})_2)]$, or $(\text{KF})_2(\text{Al}_2\text{O}_3)(\text{SiO}_2)_6(\text{H}_2\text{O})$. Still, this accounts for only some of the analytes produced during the course of the kinetic testing and is thought to be due to incomplete XRF analyses conducted at the appointed laboratory.

Possible sources of the analytes produced during the kinetic testing are given in Table 1 below. Note that these are inferred possible minerals that may have been present, with inference made from the analytes produced during the kinetic testing.

Table 1: Possible minerals present in the coal used for kinetic testing.

Mineral	Chemical composition	Analyte
Pyrite	FeS ₂	Fe; S
Chalcopyrite	Cu ₂ FeS ₂	Cu; Fe; S
Galena	PbS	Pb; S
Sphalerite	ZnS	Zn; S
Millerite	NiS	Ni; S
Covellite	CuS	Cu; S
Greenokite	CdS	Cd; S
Cinnabar	HgS	Hg; S
Pentlandite	(FeNi) ₉ S ₈	Fe; Ni; S
Bornite	Cu ₅ FeS ₄	Cu; Fe; S

5.3 Conclusion

The results emanating from this study are highlighted in the three scientific papers listed above concerning the impacts of the acid mine drainage problem in this study area. The ABA prediction methods identified geochemical characteristics of the discarded coal in the dump as potentially acid-forming (PAF). The coal discard dump acid-producing potential is greater than the acid-neutralising capacity of the coal discard dump. The kinetic column leachate testing demonstrated the quality of effluent from the coal discard during the test period of 22 weeks. This identified the quality of leachate from the dump under saturated conditions. A range of chemicals and heavy metals were identified at varying concentrations. The XRF analysis further identified the chemical composition present in the coal discard, and the XRD identified various minerals present. The river systems water quality analysis further identified a range of physical, chemical, and heavy metal parameters present in the river system to understand the

quality of the system and the compliance of the water quality to the DWS target water quality ranges. The WQI further indicated the water quality is very poor in terms of aquatic use and unfit for domestic use.

Kinetic leach tests using humidity columns were done over a 22-week period for five discard coal samples from the Indumeni Discard Dump Site which is in the Klip River Coalfields of northern KwaZulu-Natal province of South Africa. Weekly extracted leachate, containing the weathering production for this time period, was chemically analysed for pH, EC, Na, K, Al, Ca, Cu, Fe, Hg, Ni, Pb, SO₄ and Cl. Whilst some distinct patterns of analyte production and non-production was observed, the highest production rates were recorded for Sulphates followed by Ca (Carbonate equivalent). Low production rates were obtained for Na, K, Cu, Ni, Zn and Cl; moderate to high rates were obtained for EC, Fe, Hg and Al. High production rates characterised Pb, Hg and Sulphates. The cumulative mass relationship between Sulphates and Ca (carbonates) shows clear dominance of sulphates (acid production) over Ca (neutralising potential). This is further affirmed by the neutral to low pH recorded for the leachates over the 22 week testing period. The study confirmed a high potential for acid production from the discard material and this was confirmed in static testing of the same material. The implications are that there would be acid production for some time from the IDDS, hence intervention measures are required to fast-track neutralisation of acidity and so prevent contamination of both surface and subsurface water resources.

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Declaration

The authors declare no conflicts of interest.

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CHAPTER SIX

DISCUSSION AND CONCLUSION

6.1 Introduction

This chapter presents the summary of the key findings and interpretations of the results, recommendations and concluding comments concerning the prediction of acid mine drainage impact from the coal discard dump and subsequent impacts on the river systems. The three broad components of the study were the static testing conducted on the discarded coal followed by the kinetic testing and finally, the impacts on the surrounding water resources. The comprehensive study has been presented in the previous chapter as three research papers and a summary is presented herewith. Accordingly, some repetition of the information presented in those three papers is unavoidable.

6.2 Key Findings and Interpretations

6.2.1 Static Testing

The geochemical analysis of the study classified all samples as potentially acid-forming (PAF). Significant amounts of sulphur (>1%) were detected in all samples (S1 to S5) although this has not automatically translated into high acidity purely by the pH. It is also recognized that a conservative approach is using total sulphur to estimate MPA since sulphur occurs in others forms other than pyrite (not acid generating forms of sulphur e.g., sulphate sulphur. Further, some sulphites may be present as minerals other than pyrite e.g., as galena (PbS), sphalerite (ZnS), chalcocite (Cu₂S) or covellite (CuS) (AMIRA, 2002).

The total carbon analysis of the samples yielded contents of 34.68% to 60.84%. This places S2 and S3 in the bituminous class whilst the other three are classed as sub-bituminous. The organic carbon content of the samples will likely be relatively low given the long period of leaching action that the dump material has undergone. This is to be expected in a discard dump where various grades of material have been stock-piled.

The Acid Producing Potential (NAPP) values of all samples were positive and ranged from 57.64 KgH₂SO₄/t in the northern part of the dump to 92.13 KgH₂SO₄/t at S2 near the centre of the site. Interestingly, Site S5 taken at the base of the stockpile and representing the ‘ *freshest* ’

sample, recorded a NAPP of 82.19 KgH₂SO₄/t. The ANC of S3 (17.64; 1.875% CaCO₃) and S4 (31.85; 3.25% CaCO₃) would have aided in neutralizing some of the NAPP for these two sites.

The Net Acid Generation (NAG) value of more than 5KgH₂SO₄/t and all samples including the composite sample and, S3, exhibited a pH close to neutral. All samples (S1, S2, S5, and composite) were highly acidic except for S4, which has moderate acidity. All samples accordingly demonstrate low carbonate content and, where some carbonates were present (S3 and S4), the ameliorative effect on reducing acidity is evident. In the case of S1, the high acidity is aided by the presence of sulphur and a relatively high EC. The extremely high EC detected in S1 has aided in lowering pH significantly.

The NAG values ranged from 119.5 KgH₂SO₄/t. (S1) to 6.54 KgH₂SO₄/t. (S3), with S5 being 31.24. Sample S1 NAG value was higher than the NAPP value for S1. According to Pope *et al.* (2010), a NAG value higher than the NAPP value indicates that organic content reacted with sample oxidation and produced titratable organic acids. Samples containing organic material as little as 3% could significantly impact the NAG result (Pope *et al.*, 2010). Further to this Stewart *et al.* (2006), Weber *et al.* (2006), Price, (2009), Parbhakar-Fox *et al.* (2011); Parbhakar-Fox and Lottermoser, (2015), have indicated whilst this is an industry led practice, the limitation of organic matter interferes with hydrogen peroxide measurements must be carefully ensured. In addition, calcite and dolomite may react resulting in calcium hydroxide Ca(OH)₂ and alkaline pH (Stewart *et al.*, 2006, Weber *et al.*, 2006, Price, 2009, Parbhakar-Fox *et al.*, 2011; Parbhakar-Fox and Lottermoser, 2015). This is evident in samples S1 to S5, which yielded high organic matter, and the total carbon percentage ranged from 40.21% to 60.84%. The combination of the NAG and NAPP tests proved to be a better reflection of the acid mine potential of the site.

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The overall static testing results indicate significant AMD-generating potential (positive NAPP and PAF for all samples) in addition all samples yielded ANC/MPA ratios below 1, indicating a potential risk of acid generation. although the degree of acid production varies for different sites. This is related to a variety of factors including the variability of the composition of material composing the dump, the minor topographical character of the dump's upper surface that allows pooling of water in specific sites and the spontaneous combustion of parts of the dump that has been occurring for past years.

6.2.2 Kinetic Testing

The prime advantage of kinetic geochemical testing is to demonstrate the metal release or acidity rate, over a specified period due to oxidation of sulphide minerals and determining the leachate chemistry, resulting in the pollution generation rate (Davis *et al.*, 2014). In addition, Bannerjee (2014) and others have asserted that carbonate dissolution and pyrite oxidation are important chemical processes that aid identification of which suite of species has higher weathering rates – the acid producers (sulphides) or the neutralizers (carbonates).

The leachate sampling program identified five samples (five columns with coal discard) as part of the kinetic testing methodology for acid mine drainage from the leachate. The leached process was conducted over a period of 22 weeks and the following parameters were analyzed, pH, EC, Na, K, Al, Ca, Cu, Fe, Hg, Ni, Pb, SO₄ and Cl. The mean pH is indicative of the general acidic nature of the leachates. Na, K, Cu, Ni, Zn and Cl are within the acceptable mean concentration range; however, the other analytes show great variability, often in toxic concentrations.

The mean pH (5.12) recorded indicates the general acidic nature of the leachates. Column 4 maintained a near-neutral pH except at inception when there was a rapid improvement from pH 4 to neutral. Column 5 leachate was within the acceptable pH range with very noticeable weekly fluctuations. These results indicate rapid changes in acidity and neutralization of this column material with time. Column 3 displayed similar trends to Column 5 except that it commenced from acidic to neutral whereas Column 5 presented the opposite scenario. In contrast, Column 1 and Column 2 presented consistently acidic leachate (pH 3 over the entire leaching period). After the 22nd week testing period, the final pH was almost neutral for Columns 3, 4 and 5, while in Columns 1 and 2 the final pH was still approximately 3.

The sulphate concentration of Column 1 ranged from 1888.43mg/l to zero in five of the measurement weeks, with a mean concentration of 958.50mg/l. Ca concentrations remained low with mean Ca concentrations of the order of 123.07mg/l and pointed to a strong neutralizing capacity. The concentrations of analytes were assessed for their relative levels of toxicity using the South African water quality target ranges (TWQR) for aquatic (A), domestic (D) or agricultural use (AG). All other Columns yielded remarkably high Ca concentrations, exceedingly even the TWQR for domestic water use (< 32mg/l) for several of the weeks of testing. This is also shown in the mean Ca concentration (all columns) of 123.07mg/l.

The sulphate concentration declined until week eight when production began to fluctuate for all columns. Columns 3 and 4 displayed the first spike to identical concentrations of 4493mg/l in week nine. The first spike for columns 1 and 2 occurred in week ten with sulphate reaching 928.2mg/l and 3294.9mg/l, respectively. A dramatic spike in sulphates occurred in week thirteen for column 2 (6889.2mg/l), column 4 (7787.8mg/l) and Column 5 (6290.2mg/l). Column 3 yielded a sulphate concentration of 3893.9mg/l in the final week of testing. Columns 2 to 5 displayed remarkably high sulphates, ranging from 7787.8mg/l to the very few weeks when no sulphates were detected. Overall, mean sulphate concentrations far exceeded those stipulated in South African water quality standards and are in keeping with the static testing results that showed all samples as potentially acid-forming (PAF). The TWQR for domestic use of water is 0 – 200mg/l and this value was in exceedance for 79 of the total 110 weeks of testing.

Calcium (Ca) concentrations demonstrated a unique and consistent pattern for Columns 2 to 5. The period from week 14 to 19 showed a sharp decrease in concentration to < 1mg/l. Except for week 4 of Column 4, when Ca production was 1.46mg/l, the Ca production of Columns 2 to 5 recorded high Ca concentrations from inception up to week 14. The sudden and consistent low Ca for weeks 14 to 19 for all samples reflects consistency in the mineralogy of the samples. Ca production spiked for the final 3 weeks of testing; indicative of a moderate neutralizing capacity due to the rapid weathering. However, rapid weathering will also result in rapid exhaustion of the neutralizing capacity with the potential for long-term acidity to resume.

Iron production rate indicated a rapid drop from a high of approximately 0.85mg/l to zero. Concentrations of Fe were therefore low for all columns (<2mg/l). This may be attributed to

the iron-oxidizing acidophiles in the discarded coal, and the overall reduction being pH dependent (Jones *et al.*, 2015). Fe, concentrations were within the TWQR (AG: 0-10mg/l) but did exceed the domestic standards ($< 0.1\text{mg/l}$) for Column 1 (13 weeks) and Column 2 (19 weeks). Overall mean Fe concentrations (1.01mg/l) would render the water unfit for domestic use.

Nickel production for all columns was below the upper limit of TWQR for Ni (AG) is 0 – 2 mg/l and therefore of no concern to the receiving environment. However, Pb production (TWQR = 0.001 – 0.2) was high for all Columns and all weeks except the period week 14 to 19. The mean Pb production was 0.76mg/l which exceeds the upper TWQR (A). The total Ni production was 15.13mg/l with a mean of 3.03mg/l whilst the total Pb production was 36.16mg/l with a mean of 7.23mg/l .

Copper production yielded low concentration output throughout the leaching tests. A slight anomaly is seen at week eleven for Column 3 when concentration reached 0.19mg/l , week 13 for Column 1 (2.15mg/l) and week 20 for Column 2 (2.54mg/l). These three values exceeded the TWQR (D) $< 2\text{mg/l}$. Additionally observed was the decrease in Cu production rate from week 14 to 19.

The sodium (Na) concentration release (columns 1 to 5) was consistent at 3 to 7mg/l during the testing period, with minor fluctuations. The constant release of Na is directly related to the state in which Na occurs in coal. According to Wang *et al.* (2024), Na is present in coal in a water-soluble state, largely ($>70\%$) in a hydrated state as $\text{H}_2\text{O-Na}$. This implies that minerals randomly distributed within the coal are not the primary sources of Na. Instead, the Na when present, is homogeneously distributed within the coal seam. Hence, ongoing weathering will release sodium in a constant concentration over time.

Throughout the leaching test conducted for columns 1 to 5 potassium (K) displayed consistently low concentrations with minor fluctuations and remained below the TWQR of $<50\text{mg/L}$. Potassium is known to occur in the clay mineral illite (Spiro *et al.*, 1986), its release is related to the presence of illite in each of the columns. The minor spikes shown in the production curves for K are indicative of the weathering of these specks of clay minerals in the samples.

Aluminum displayed high production rates in Columns 1 and 2 (4.93mg/l total and 97.87mg/l respectively) exceeding both the aquatic and agricultural TWQR for Al (< 5mg/l) and are therefore likely to create negative impacts on the natural environment. In a similar vein, Al displayed a similar trend to Ni and Pb in demonstrating a fall-off in production rates for weeks 14 to 19.

The production of Cl was well below the TWQR of <200mg/l for all columns ranging between 20 and 120mg/l with regular fluctuations from week to week and is therefore not a potential threat of contamination following long-term weathering of the coal. Contamination may however still occur through concentration in water bodies.

The production of Mercury (Hg) followed a unique path compared to the other analytes. Initially, some Hg was produced, like due to Galena dissolution. For a six-week period, there was minimal production of HG (<0,7mg/l) from Column 5 and none from the other columns. Thereafter, production resumed from all columns, reaching a peak concentration of just over 5mg/l for all columns. The only exception is Column 4 where the highest concentration of 9.48mg/l was recorded. Domestic standards require Hg concentrations to be below 0.000001mg/l and the concentrations yielded reached toxic levels in terms of the TWQR standards.

The electrical conductivity (EC) measurements initially indicated a rapid drop off for the first two weeks to approximately 200mS/m for columns 2 – 5 except Column 1 which maintained extremely low levels throughout the test duration. Thereafter a very gradual decline to approximately 150mS/m was observed. This pattern is expected given the gradual overall decline in the production of analytes over the leach test period.

In addition, cumulative rates of sulphate and carbonate weathering were determined. It is evident the rate of sulphate production far exceeds that of carbonates, demonstrating the low neutralizing capacity overall. The relation between the acidification and neutralization products indicates that the oxidizing capacity exceeds the neutralizing capacity by a ratio of up to 10:1. This ratio could be an overestimate as not all neutralizing agents were assessed. However, static testing on the same samples did confirm the potentially acid-forming character of all five samples used in this series of kinetic tests.

The overall kinetic testing results indicate significant leachate contamination from the parameters analysed thus indicating the acid generation risk potential. This is related to the age of the dump, variability of the composition of material composing the dump, the instantaneous combustion occurring of parts of the dump that have been occurring for several years and the varying atmospheric conditions experienced.

6.2.3 XRF Analysis and Other Mineralogical Sources

The mineralogical characteristics of the samples determined with XRF and XRD analysis indicated the composite sample (CS), S2, S4, and S5 were found to contain quartz, kaolinite/dickite, illite/muscovite and gypsum while both Samples 1 and 3 contained quartz, kaolinite/dickite and gypsum. The highest crystallinity index observed is ~74% with S1 and S3 showing the highest amorphous content (lowest crystallinity index). This may contribute to the neutralising capacity with the presence of gypsum in addition to the amorphous content. This analysis shows that the detrital material incorporated into the discarded coal is unlikely to generate additional acidity. No pyrite or other acid-generating minerals were detected, and this is assumed to be a consequence of the advanced state of chemical decomposition of these minerals.

The chemical composition as determined by XRF indicated the following: the composite sample (S1 to S5) contained very high amounts of Ba (453.17ppm), Sr (360.80ppm) and Zr (127.08ppm); moderately high amounts of V and Ce (30 – 99 ppm); moderate amounts (20 – 30 ppm) of Cr, Cu, Y and La; and, low Sc, Y, Gd, Tb, Ho, Yb, Lu, Hf, Co, Dy, Er, Eu, La, Mo, Ni, Nd, Nb, Pb, Pr, Rb, Sm, Ta, Th, U and Zn. Evidently some trace elements in coal are radioactive, these include uranium (U) and thorium (Th), (Papastefanou, 2010; Singh *et al.*, 2015) thus presenting a health risk to the population (Singh *et al.*, 2015). The evidence of the radioactive elements results from the instantaneous combustion producing flyash at the coal discard dump site. Singh *et al.* (2015), and others have further documented this in other studies.

The potential adverse chemical characteristics of the flyash and impacts into the water systems and the environment will lead to potential toxic substances leaching into groundwater and soils (Carlson and Adriano, 1993). Ultimately reducing the formation and growth of plant species, changes in the primary composition of vegetation growth on the ash; as well as increased accretion and mobility of the potentially toxic elements (Carlson, and Adriano, 1993).

Increased levels of Ba in drinking water can result in several health impacts with the most serious being the negative impacts to the urinary system (DWAF, 1996). However, Ba is easily removed in water treatment. Zr on the other hand, has detrimental impacts to biota in the natural environment and should be kept below contamination levels in water systems. Both V and Ce occur in high concentrations in the composite coal and are a danger to the natural environment.

The exceptionally high amount of Sr found in the discarded coal composite sample points indicates relatively long ageing and, in turn, possible further long-term leaching to, and contamination of, surrounding water resources. The possible health effects with reference to excess Sr are related to the similarity of the latter to Ca and Mg and its possible replacement in bone tissue leading to bone cancers (DWS, 1996).

Cu, Cr, Pb, Mn, Zn and Ti are minor and trace elements which are partly or fully water-insoluble (Spivak-Birndorf *et al.*, 2012) are associated with phosphates, clay minerals and other detrital minerals which has association with more refractory phases in coal (Swaine, 1990; Izquierdo *et al.*, 2011) thought to transform in part to aluminosilicate glass and other compounds in combustion (Mattigod *et al.*, 1990; Spivak-Birndorf *et al.*, 2012). Sr, Ba, Be, Co, Cr, Mo, Pb, and Zn are the main elements that readily accumulate in coal ash (Vejahati *et al.*, 2010) and Ba, Ca, Mg, Na and Sr decrease in concentration with coal rank (Lindahl and Finkelman, 1986; Swaine, and Goodarzi, 2013).

The overall classification of the coal discard dumps indicated non-acid-forming minerals, this is attributed to pyrite and other acid-producing minerals not being detected. On the other end, the coal discard chemical composition indicated toxic levels of trace metals and radioactive elements including uranium (U) and thorium (Th), which is detrimental to the environment.

6.2.4. Water Quality Analysis

The physiochemical parameters of the river water samples were benchmarked against the DWS Water Quality Guidelines for Aquatic Ecosystems. In the absence of a target water range (TWQR) in the aquatic ecosystem guideline, the domestic and agricultural water quality guideline was adopted to determine fitness for use.

The chloride (Cl) concentrations indicated that 27% of the samples exceeded the TWQR, falling within the unacceptable chronic effect value (CEV) range, and acute effect value (AEV)

range. The observed fluctuations of Cl in surface water result from various industrial processes, sewage effluent discharges and irrigation return flows (DWAF, 1996a).

The electrical conductivity (EC) results indicated that 45% of the samples exceeded the threshold of the TWQR and fell within the tolerable, chronic, and acute effect value ranges, the latter with elevated unacceptable limits. According to DWAF (1996a), electrical conductivity concentrations ranging from 150-300 mSm have a marked salty taste, as a result, this would not be used on aesthetic grounds if availability of other suppliers were applicable. Whilst no health effects are noticeable at this range, health effects are noticeable at 300mSm and above. The increase in electrical conductivity is attributed to the iron-enriched leachate from the coal discard dump.

The potassium (K) concentrations accounted for 55% of the samples being within the threshold of the TWQR and deemed acceptable whilst 54% of the sodium (Na) results exhibited elevated levels and were in exceedance of the TWQR. Metabolically sodium interacts with potassium and are most significant extracellular and intracellular cations that are vital for all living organisms (DWAF, 1996a) health effects are noticeable at sodium concentrations above 600mg/L. According to DWAF (1996a), the levels of sodium concentrations in the surface are generally low however, in this study, significant sodium concentrations are noted.

Aluminium (Al) concentrations observed in 61% of the samples ranged within the chronic (CEV) and acute effect value (AEV) ranges. This interaction is strongly influenced by pH DWAF (1996a), Aluminium is found in soluble forms in acid mine drainage water and is among the principal particulates emitted from coal combustion. This high concentration relates to high Al concentration from the leachate sample in the kinetic test. The elevated levels of bio-available aluminium in water are toxic to a variety of aquatic organisms (DWAF, 1996c). Whilst there is some uncertainty in terms of the level of toxicity, effects are dependent on the species and life stage of the organism (DWAF, 1996).

Cobalt (Co) was not detected, in contrast, Sulphates (SO_4), Nickel (Ni), and Calcium (Ca), on were within the TWQR and categorised into the acceptable range. Cd concentration accounted for 60% of the results in exceedance of the TWQR and fell within the chronic and acute effect value ranges. Fifty-five percent of the copper (Cu) and chromium (Cr^{6+}) samples exceeded the

acute effect value (AEV). According to DWAF (1996c), 90% of all Cr^{6+} values need to be within the TWQR to ensure the protection of the aquatic system, however, in exceedance, Cr^{6+} exerts toxic effects at different concentrations among different aquatic biota.

Iron (Fe) concentrations in the river system were within the TWQR and tolerable limit range, similarly Fe concentration from the leachate of the coal discard were within the TWQR, a clear indication that Fe has no adverse impact to the system. Mercury (Hg) concentrations of 45% exceeded the TWQR and fell within the acute effect value range (AEV) and above whilst 46% of the samples showed Ni concentrations that were within the TWQR. Whilst Cu and Cr had the highest exceedance of the AEV from all parameters assessed, Pb (27%) and Zn (36%) were within the chronic and acute effect range exhibiting extremely elevated levels.

A Spearman's rank correlation test indicated that all physiochemical parameters were found to be statistically significant with a strong, positive correlation for pH, EC, TDS, Na, K and Cl. Various processes from both natural weathering and anthropogenic sources contribute to the addition of Na, K and Cl ions into natural water systems.

A Kruskal-Wallis and a Mann-Whitney U post-hoc test was performed to determine if parameters differ significantly based on the location of sites relative to the IDSS. Both tests indicated significant, positive correlations between pH, EC, TDS, Na, K and Cl.

The distributional character of contaminants was further analysed by a Kruskal-Wallis test. This showed statistically significant differences for all physicochemical parameters including; pH, TDS, EC, K, Na and Cl ($p < 0.001$) and for metals; Al, Ca, Cr, Cu, Fe, Hg, Ni, Pb, Zn, SO_4 ($p < 0.05$), except for Cd ($p > 0.05$) which was not significantly different among the five sampling sites.

A post-hoc Mann-Whitney U test indicated the differences between each site yielding multiple site pairs with significant differences for both physico-chemical and, metal parameters respectively. pH was significantly different ($p < 0.005$) between site 1 and all other sites, shown by pairs (1-2), (1-3), (1-4), (1-5). EC was significantly different ($p < 0.005$) for site pairs (2-4) and (2-5) while TDS differences were found for site pairs (2-4) and (2-5). Cl had significant differences for site pairs ($p < 0.005$) (2-4) and (2-5). K was significantly different for pairs (2-

3), (2-4) and (2-5) and Na was found to be different for (2-4). Ca, Cr and Ni were significantly different ($p < 0.005$) between site pairs, (1-2), (1-3) and (1-5). A significant difference was found for Al, Hg, and SO_4 among five of the following site pairs, (1-2), (1-3), (1-5), (2-4), (4-5). Cu had significant differences for ($p < 0.005$) at sites: (1-2), (1-3), (1-4), (1-5), (2-4). Lastly, Pb had one site pair (1-2) which was found to be significantly different while Zn exhibited a significant difference for site pairs, (1-2) and (2-4).

The site pair that displayed the maximum number of parameters exhibiting significant differences was between site 1 and all other sites. This is particularly stark between site 1 and site 2 with 16 parameters including pH, EC, TDS, Na, K, Cl, Al, Ca, Cr, Cu, Fe, Hg, Ni, Pb, Zn and SO_4 . Site 1 is located upstream of the IDDS not directly impacted by the discard dump. This is especially true of the differences between sites 1 and 2, the latter being most immediately impacted by leachate from the discard dump. This is also evidenced by the presence of ferric hydroxide (yellow boy) observed in site 2, this is an indication of acid mine drainage characteristics which has contributed to this result. Site 1 and site 3 had 14 parameters which were significantly different as well as site 1 and site 5. This included pH, EC, TDS, Na, K, Cl, Al, Ca, Cr, Cu, Fe, Hg, Ni, SO_4^{2-} subsequently outlining the impact level on the aquatic system. Site 3 to site 4 was the only combination along the study area which yielded statistically significant differences for any of the parameters and may be related to natural attenuation. While there is a decrease of means between these sites, there were occasions at site 4 when there was no flow due to prolonged winter dry periods. This suggests that parameter concentrations from site 1 to site 2 have a meaningful difference which could be a result of the adjacent environment at each site. Notably, three sites (Sites 3, 4 and 5) had fewer parameters of significance, indicating that ions in solution may be inhibited or potentially experience dilution downstream. Marove *et al.*, (2022) emphasize that coal discarded materials are naturally contaminated with inorganic constituents. Additionally, Vejehati *et al.*, (2010) note that trace elements are available in the coal ash, indicating that the coal discard dump was impacted by instantaneous combustion. These trace elements were detected in varying concentrations through XRF analysis on the coal discarded material as detailed in a paper entitled: *The characterization of Acid Mine Drainage using Static Testing at the abandoned*

Indumeni Discard Dump Site, uThukela Water Management Area, KwaZulu-Natal, South Africa.

The Water Quality Index (WQI) provides a general assessment of water quality and is applied in various ways depending on the use that the assessment is intended for. The strength of this test is the ability to consider the comprehensive set of parameters and provide a generic categorization of the water quality (Akkaraboyina and Raju, 2012). This in turn can be used to assess the ability of a water resource to support aquatic biota or whether the overall quality poses any threat to other water uses (Akkaraboyina and Raju, 2012). The average WQI of S1 ranges from 61.59 (poor water quality) at Site 1 located upstream of the IDDS, to 208.42 at S2 (unfit for domestic use) immediately downstream of the discard dump site. It is clear from this result alone that the discard dump is contributing a significant number of contaminants to the river system through leaching processes. Interestingly, there is an increase in water quality from Site 3 (WQI = 174.52) to Site 4 (WQI = 150.32) to Site 5 (WQI = 75.23). This is probably due to some sequestration of contaminants with increasing distance from the discard dump site. Nevertheless, the water quality at these sites is still unacceptably high, ranging from unfit for domestic use (S2, S3 and S4) to very poor (S1 and S5). This issue is linked to the legacy impacts of surface and groundwater pollution emanating from the abandoned mines in this catchment. Hence follow-up studies that incorporate the role played by surrounding land uses should be undertaken.

The WQI assessment shows that the overall surface water quality at the five sites is poor to very poor. Specific reference is made to the water quality at Site 2, just downstream of the IDDS is categorised as unfit for domestic use indicating contamination directly from the dumpsite. This finding aligns with the results from the kinetic leachate testing of the coal discard which, reveals elevated metal concentrations and high acidity. Sample sites 3, and 4 are further deemed unfit for domestic use. Although the actual coal discard dump in the vicinity of the resources does play a role in the pollution contribution, it is not solely responsible for the pollution of the river system, but rather a contributor to the overall pollution issues.

Overall, the elevated levels of physiochemical and heavy metals have contributed to the polluted state of the river systems, resulting in the water quality being considered unfit for use and impacting the aquatic biota and environment. This situation observed from the assessment

can be attributable to historical mining-related activities and inadequate mine water pollution control in the study area.

6.3 Recommendations

- The National Government is advised to address the gaps that exist in the current legislative framework relating to abandoned mines (Kuipa, 2023; Kuipa and Lekunze, 2024). This is preventing abandoned mine rehabilitation and subsequent protection of water resources in the study area.
- The rehabilitation of this coal discard dump should be recognised as top priority from the National Government for the possible rehabilitation of the discard dump. Previously this dump formed part of the defunct mine rehabilitation project in the Sandspruit catchment, KwaZulu-Natal (DWS, 2014).
- An interministerial task team may assist with identification of all social, environmental, and financial risk associated with this coal dump as well as the impact of the decanting acid mine water into the water resources. The results from this investigation should possibly be presented to DWS and other governmental departments to solicit funding for the rehabilitation of this abandoned mine.
- Rehabilitation of the coal discard dump should focus on the transformation of carbonaceous waste into material of soil-like nature via biotic and abiotic methods as well as vegetation cladding of the dump and/or opencast spoil (Cowan, *et al.*, 2016). This will assist in the land restoration of the affected mined area.
- The current pollution control dam and the associated infrastructure to the final discharge point require on going operation and maintenance to meet the water quality discharge limits. This may be assisted by the National Government.
- Robust monthly water quality monitoring of the following: decant water filling into the pollution control dam, the final effluent exiting the pollution control system, the upstream borehole site, downstream borehole site and sediment sample from the pollution control dam should be conducted.
- Effects should be made to treat the contaminated water in the pollution control dam downstream of the coal discard dump. A treatment facility may be erected to treat the

water before returning to the river system or supplement downstream uses for agricultural use.

- Aquatic biomonitoring to be implemented for determining the current health status of the affected water resources in the study area.
- Due to the instantaneous combustion occurring at the dump site, air quality monitoring to be implemented to ascertain air pollution levels of the area.
- Currently the discard dump is being re-mined, which will reduce the tonnage of the discard material on site, however extensive erosion has taken place. This requires shaping and contouring of the coal dump.
- There is no proper stormwater and pollution control evident onsite. This further leads to polluted water run-off into the environment. Proper stormwater control should be implemented to prevent further pollution on site and into the river system.
- Proper access control measures and improvement of demarcation to be implemented at the site for the safety and wellbeing of the surrounding community and livestock.
- To ensure the sustainable management of residual and latent environmental risks at the coal discard dump, rehabilitation in terms of post mining land adaptive management (Mineral Council of South Africa, 2018) would need to take place in line with the National Strategy for the Management of Ownerless and Derelict mines in South Africa (DMR. 2009).

6.4 Conclusion

The geochemical assessment of acid mine drainage and water quality within the study area have clearly indicated the ability of the coal discard dump to be potentially acid forming and the current chemical composition of the dump as well as the fitness of use of the water quality of the river system determined. This study area is highly polluted with water not fit for both domestic and aquatic use and requires urgent attention from all spheres of government for the protection and sustainable use. It is therefore recommended that further investigations be conducted, and that comprehensive mine waste management plan and mine water management control be established and implemented in this catchment area to protect water resources for the aquatic biota, livestock, agricultural and domestic use.

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APPENDIX 1.1
Kinetic leachate results (Column 1 and Column 2)

Sample Date (Column 1)	pH	EC (mS/m)	Na (mg/L)	K (mg/L)	Al (mg/L)	Ca (mg/L)	Cu (mg/L)	Fe (mg/L)	Hg (mg/L)	Ni (mg/L)	Pb (mg/L)	SO ₄ (mg/L)	Cl (mg/L)
Week 1	3.1	5030	7.75	0.26	19.07	8.07	1.71	20.96	7.30	1.04	1.15	1287.63	130.4
Week 2	2.76	62.5	3.27	0.20	0.17	1.63	0.55	0.13	0.07	0.19	0.10	691.63	19.14
Week 3	2.46	87.9	5.19	0.29	0.17	5.11	0.43	0.09	0.00	0.18	0.06	478.3	30.95
Week 4	2.51	94.4	3.05	0.29	0.18	8.47	0.35	0.16	0.00	0.19	0.22	128.64	43.24
Week 5	2.49	71	4.36	0.07	0.27	2.49	0.32	0.66	0.00	0.12	0.12	112.7	39.7
Week 6	2.56	69.15	3.22	0.14	0.15	3.65	0.65	0.22	0.00	0.15	0.26	88.69	39.02
Week 7	2.64	51.1	4.69	0.05	0.17	1.01	0.29	0.14	0.00	0.12	0.38	317.62	45.13
Week 8	2.59	60.4	7.01	0.43	0.21	4.36	0.32	0.20	0.00	0.15	0.29	77.68	75.15
Week 9	2.7	50.5	4.78	0.16	0.16	0.44	0.23	0.09	0.00	0.13	0.50	119.8	56.56
Week 10	2.66	49.5	4.29	0.19	0.15	0.68	0.21	0.07	0.00	0.13	0.29	928.6	40.64
Week 11	2.7	43.6	5.09	0.66	0.18	0.55	0.19	0.11	0.00	0.13	0.42	77.9	78.22
Week 12	2.74	43.1	4.94	0.10	0.49	3.33	0.54	0.24	1.34	0.19	0.47	56.9	61.21
Week 13	2.68	42.7	4.05	0.08	0.32	5.26	2.15	0.23	1.26	0.18	0.26	898.6	56.72
Week 14	3.14	15.89	4.47	0.04	0.24	1.47	0.08	0.12	1.35	0.16	0.00	0.00	45.84
Week 15	3.09	18.25	3.67	0.27	0.22	0.48	0.07	0.11	1.47	0.16	0.00	0.00	30.01
Week 16	3.06	19.47	4.70	0.44	0.17	0.83	0.07	0.01	0.61	0.10	0.00	0.00	40.88
Week 17	2.7	41.2	4.61	0.56	0.17	0.83	0.07	0.01	1.11	0.10	0.00	47.9	32.37
Week 18	2.71	37.3	4.51	0.06	0.18	0.83	0.06	0.00	5.17	0.10	0.00	24.6	43.24
Week 19	2.73	34.9	5.77	0.12	0.18	0.83	0.06	0.07	5.26	0.00	0.00	0.00	53.64
Week 20	2.8	35.5	4.42	0.11	0.20	2.97	0.29	0.20	0.00	0.10	1.38	206.7	39.7
Week 21	2.76	35.6	5.65	0.08	0.31	10.43	0.37	0.58	0.00	0.11	1.48	23.1	43.25
Week 22	3.03	38.9	2.54	1.95	0.24	3.38	0.39	6.34	0.26	0.14	1.38	0.00	57.19

Sample (Column 2)	pH	EC (mS/m)	Na (mg/L)	K (mg/L)	Al (mg/L)	Ca (mg/L)	Cu (mg/L)	Fe (mg/L)	Hg (mg/L)	Ni (mg/L)	Pb (mg/L)	SO ₄ (mg/L)	Cl (mg/L)
Week 1	2.13	445	5.44	0.21	132.90	266.47	3.78	69.21	0.00	2.29	0.64	1882.58	65.46
Week 2	3.54	132.8	4.64	0.08	5.32	187.93	0.02	0.21	1.73	0.22	0.00	619.67	42.77
Week 3	3.06	145.2	5.04	0.06	7.38	190.97	0.03	0.40	2.04	0.23	0.00	1041.86	33.55
Week 4	3.18	148.2	3.18	0.07	7.10	203.33	0.07	0.42	2.03	0.25	0.06	1012.73	45.84
Week 5	3.2	149.2	3.64	0.05	5.54	157.73	0.18	0.34	0.00	0.19	0.00	312.46	24.81
Week 6	3.04	159.4	3.13	0.08	6.21	167.89	0.12	1.04	0.00	0.20	0.00	958.86	34.73
Week 7	3.01	164.2	4.76	0.03	5.32	163.80	0.21	0.38	0.00	0.20	0.38	974.17	45.61
Week 8	2.88	177.7	6.28	0.23	7.12	165.93	0.12	0.53	0.00	0.21	0.00	852.9	56.24
Week 9	2.96	172.4	5.27	0.05	4.80	125.60	0.11	1.06	0.00	0.17	0.00	2126.7	33.95
Week 10	2.98	162.4	4.87	0.17	4.21	118.03	0.11	0.40	0.00	0.15	0.00	3294.9	56.01
Week 11	3.04	159	4.88	0.07	3.50	109.63	0.09	0.31	0.00	0.17	0.19	2036.8	44.43
Week 12	3.03	159	5.25	0.02	6.10	183.37	0.21	0.95	1.71	0.25	0.23	1048.4	38.28
Week 13	2.9	157.3	4.64	0.01	5.08	164.90	0.20	0.62	1.50	0.23	0.30	6889.2	39.46
Week 14	3.15	137.9	6.12	0.03	0.22	0.44	0.08	0.12	1.21	0.16	0.00	1228.1	30.72
Week 15	3.45	166.2	4.96	0.11	0.21	0.33	0.07	0.11	1.36	0.16	0.00	2635.90	34.15
Week 16	2.89	149.1	4.59	0.10	0.17	0.83	0.07	0.02	1.90	0.10	0.00	0.00	38.75
Week 17	2.94	148.1	4.87	0.04	0.17	0.83	0.07	0.00	2.68	0.10	0.00	778.80	39.46
Week 18	2.95	152	4.97	0.00	0.18	0.83	0.06	0.00	5.09	0.10	0.00	0.00	49.39
Week 19	2.95	147.3	6.04	0.05	0.18	0.83	0.06	0.06	5.04	0.00	0.00	569.10	40.64
Week 20	3.04	151	5.27	0.03	3.84	529.78	2.54	1.04	0.05	0.13	0.86	212.70	55.53
Week 21	3.01	150	5.27	0.05	3.57	547.72	0.56	0.97	0.55	0.13	1.02	0.00	46.08
Week 22	3.15	191.5	3.06	0.14	4.80	684.44	0.13	0.97	0.00	0.13	0.82	0.00	65.93

DWS Water Quality Guidelines: Green-Target water quality range, Yellow-Tolerable range, Orange-Chronic effect range, Red-Acute effect range.

APPENDIX 1.2

Kinetic leachate results (Column 3 and Column 4)

Sample Date (Column 1)	pH	EC (mS/m)	Na (mg/L)	K (mg/L)	Al (mg/L)	Ca (mg/L)	Cu (mg/L)	Fe (mg/L)	Hg (mg/L)	Ni (mg/L)	Pb (mg/L)	SO ₄ (mg/L)	Cl (mg/L)
Week 1	3.1	5030	7.75	0.26	19.07	8.07	1.71	20.96	7.30	1.04	1.15	1287.68	130.4
Week 2	2.76	62.5	3.27	0.20	0.17	1.63	0.55	0.13	0.07	0.19	0.10	691.63	19.14
Week 3	2.46	87.9	5.19	0.29	0.17	5.11	0.43	0.09	0.00	0.18	0.06	478.3	30.95
Week 4	2.51	94.4	3.05	0.29	0.18	8.47	0.35	0.16	0.00	0.19	0.22	128.64	43.24
Week 5	2.49	71	4.36	0.07	0.27	2.49	0.32	0.66	0.00	0.12	0.12	112.7	39.7
Week 6	2.56	69.15	3.22	0.14	0.15	3.65	0.65	0.22	0.00	0.15	0.26	88.69	39.02
Week 7	2.64	51.1	4.69	0.05	0.17	1.01	0.29	0.14	0.00	0.12	0.38	317.62	45.13
Week 8	2.59	60.4	7.01	0.43	0.21	4.36	0.32	0.20	0.00	0.15	0.29	77.68	75.15
Week 9	2.7	50.5	4.78	0.16	0.16	0.44	0.23	0.09	0.00	0.13	0.50	119.8	56.56
Week 10	2.66	49.5	4.29	0.19	0.15	0.68	0.21	0.07	0.00	0.13	0.29	928.6	40.64
Week 11	2.7	43.6	5.09	0.66	0.18	0.55	0.19	0.11	0.00	0.13	0.42	77.9	78.22
Week 12	2.74	43.1	4.94	0.10	0.49	3.33	0.54	0.24	1.34	0.19	0.47	56.9	61.21
Week 13	2.68	42.7	4.05	0.08	0.32	5.26	2.15	0.23	1.26	0.18	0.26	898.6	56.72
Week 14	3.14	15.89	4.47	0.04	0.24	1.47	0.08	0.12	1.35	0.16	0.00	0.00	45.84
Week 15	3.09	18.25	3.67	0.27	0.22	0.48	0.07	0.11	1.47	0.16	0.00	0.00	30.01
Week 16	3.06	19.47	4.70	0.44	0.17	0.83	0.07	0.01	0.61	0.10	0.00	0.00	40.88
Week 17	2.7	41.2	4.61	0.56	0.17	0.83	0.07	0.01	1.11	0.10	0.00	47.9	32.37
Week 18	2.71	37.3	4.51	0.06	0.18	0.83	0.06	0.00	5.17	0.10	0.00	24.6	43.24
Week 19	2.73	34.9	5.77	0.12	0.18	0.83	0.06	0.07	5.26	0.00	0.00	0.00	53.64
Week 20	2.8	35.5	4.42	0.11	0.20	2.97	0.29	0.20	0.00	0.10	1.38	206.7	39.7
Week 21	2.76	35.6	5.65	0.08	0.31	10.43	0.37	0.58	0.00	0.11	1.48	23.1	43.25
Week 22	3.03	38.9	2.54	1.95	0.24	3.38	0.39	6.34	0.26	0.14	1.38	0.00	57.19

Sample (Column 4)	pH	EC (mS/m)	Na (mg/L)	K (mg/L)	Al (mg/L)	Ca (mg/L)	Cu (mg/L)	Fe (mg/L)	Hg (mg/L)	Ni (mg/L)	Pb (mg/L)	SO ₄ (mg/L)	Cl (mg/L)
Week 1	4.28	270	9.11	0.85	1.04	187.83	0.13	0.10	0.00	0.23	7.75	1766.85	73.02
Week 2	6.4	132.1	6.64	0.29	0.20	202.70	0.00	0.19	0.47	0.20	0.44	907.09	24.34
Week 3	6.64	131.8	6.17	0.33	0.13	129.98	0.00	0.06	0.50	0.18	0.35	777.64	34.03
Week 4	6.68	133.1	5.85	0.33	0.19	1.46	0.09	0.09	0.00	0.12	0.22	996.3	53.88
Week 5	6.82	123.8	5.85	0.25	0.13	140.37	0.07	0.06	0.00	0.14	0.80	956.49	42.54
Week 6	6.86	134.3	6.11	0.47	0.14	108.21	0.02	0.06	0.00	0.14	0.56	942.06	39.11
Week 7	6.85	134.6	6.04	0.24	0.12	130.07	0.03	0.06	0.00	0.12	0.67	543.65	68.77
Week 8	6.99	147.6	6.87	0.32	0.14	140.70	0.04	0.06	0.00	0.15	0.89	504.38	49.72
Week 9	7.21	135.2	5.86	1.37	0.13	106.71	0.03	0.05	0.00	0.14	0.47	4493	35.45
Week 10	7.24	137	6.13	1.67	0.13	116.10	0.03	0.05	0.00	0.15	0.57	539.2	59.08
Week 11	7.15	136.3	6.12	0.19	0.13	106.33	0.03	0.05	0.00	0.14	0.60	329.5	53.41
Week 12	7.1	129.1	4.76	0.20	0.21	169.20	0.12	0.17	0.83	0.20	0.37	359.4	68.53
Week 13	7.06	129.8	5.78	0.02	0.22	1.82	0.08	0.12	1.48	0.16	0.00	7787.8	53.17
Week 14	7.19	127.1	5.26	1.24	0.22	0.40	0.08	0.12	1.05	0.16	0.00	1303	39.7
Week 15	7.44	118.9	5.27	0.14	0.21	0.32	0.07	0.11	0.86	0.16	0.00	838.7	43.72
Week 16	7.38	125.5	5.52	0.21	0.17	0.83	0.07	0.01	1.65	0.10	0.00	1288	49.15
Week 17	7.37	122.8	5.53	0.19	0.17	0.83	0.06	0.00	4.59	0.10	0.00	1917	35.21
Week 18	7.3	120.9	5.62	0.16	0.18	0.83	0.06	0.07	5.20	0.07	0.00	284.6	35.45
Week 19	7.17	118	5.92	0.19	0.18	0.83	0.06	0.06	5.01	0.00	0.00	389.4	52.7
Week 20	7.44	122.8	6.30	0.19	0.17	464.71	0.11	0.12	9.48	0.12	1.32	329.5	43.72
Week 21	7.52	116.3	6.30	0.33	0.16	484.87	0.10	0.13	0.00	0.11	1.36	3893.9	49.63
Week 22	7.23	155.9	4.45	0.10	0.16	648.15	0.09	0.13	0.00	0.12	1.69	299.5	71.84

APPENDIX 1.3

Kinetic leachate results (Column 5)

Sample (Column 5)	pH	EC (mS/m)	Na	K	Al	Ca	Cu	Fe	Hg	Ni	Pb	SO ₄	Cl
Week 1	8.78	335	12.05	3.16	0.48	229.77	0.35	0.85	0.00	0.38	20.29	1910.76	0.00
Week 2	8.04	212	7.02	0.55	0.16	233.54	0.00	0.21	0.00	0.19	0.26	1080.38	52.46
Week 3	7.90	205	5.41	0.57	0.12	327.50	0.00	0.07	0.93	0.20	0.42	816.7	59.73
Week 4	8.00	196	4.31	0.55	0.11	240.70	0.04	0.07	0.00	0.14	0.25	1044.22	54.59
Week 5	7.98	197	5.33	0.47	0.12	227.43	0.04	0.07	0.00	0.13	0.70	1034.14	75.62
Week 6	6.78	177	5.20	0.72	0.12	205.24	0.01	0.07	0.00	0.15	0.47	1037.79	62.1
Week 7	5.4	159	5.31	1.45	0.13	174.27	0.04	0.07	0.00	0.14	0.46	227.53	47.26
Week 8	5.75	159	5.76	0.47	0.14	148.47	0.05	0.09	0.00	0.14	0.64	996.81	56.95
Week 9	5.7	149	5.09	0.83	0.13	113.09	0.04	0.05	0.00	0.13	0.37	1258	78.46
Week 10	6.78	132.8	5.34	0.92	0.13	101.89	0.03	0.05	0.00	0.11	0.33	659	57.66
Week 11	6.78	129.1	5.27	0.24	0.14	103.09	0.03	0.05	0.00	0.11	0.52	137.8	48.44
Week 12	5.61	128.2	5.07	0.17	0.22	166.33	0.12	0.18	1.55	0.18	0.30	958.5	53.17
Week 13	6.33	115.3	4.64	0.12	0.21	0.29	0.07	0.12	1.44	0.16	0.00	6290.2	60.26
Week 14	6.86	111.2	4.36	1.42	0.22	0.70	0.08	0.12	1.34	0.16	0.00	713.05	43.48
Week 15	7.88	107.9	5.62	2.09	0.22	0.36	0.07	0.11	1.11	0.16	0.00	539.2	39.23
Week 16	4.36	108.6	5.00	0.31	0.17	0.83	0.07	0.01	0.80	0.10	0.00	1198.1	53.41
Week 17	5.26	105.2	5.12	0.25	0.17	0.83	0.06	0.00	5.37	0.10	0.00	0.00	52.93
Week 18	6.22	99.3	5.39	0.22	0.17	0.83	0.06	0.06	5.04	0.00	0.00	182.7	48.44
Week 19	6.8	95.8	6.64	0.22	0.17	116.17	0.07	0.08	4.86	0.05	0.00	209.7	40.88
Week 20	6.86	94.6	6.14	0.22	0.16	358.87	0.10	0.12	0.00	0.11	1.00	1347.9	33.55
Week 21	7.03	91.6	6.14	0.32	0.16	398.91	0.10	0.12	0.00	0.11	1.34	59.9	35.21
Week 22	7.41	111.7	3.27	0.34	0.16	450.28	0.09	0.12	0.00	0.11	0.58	179.7	52.23

APPENDIX 2.1

River Water Quality Sampling Results (November 2017 – February 2020)

Date	Site No.	pH	EC(mS/m)	TDS	Na (average)	K(average)	Al (average)	Ca (average)	Cd (average)	Co (average)	Cr (average)	Cu (average)	Fe (average)	Hg (average)
20/11/17	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	9,24	273,09	24251,37	857,61	10,23	0,189	57,148	ND	ND	0,456	0,107	0,165	4,557
	3	8,98	273,85	15460,64	761,95	3,41	<0,1	30,255	ND	ND	0,455	0,099	0,139	2,232
	4	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	5	8,32	28,79	1871,87	97,08	2,96	2,284	18,761	ND	ND	ND	0,103	2,698	4,322
14/12/17	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,93	108,28	7038,72	194,68	6,28	0,229	28,106	ND	ND	0,611	0,099	0,2	2,425
	3	8,68	131,45	8544,83	258,53	4,04	0,192	28,608	ND	ND	1,175	0,091	0,222	4,709
	4	8,77	157,46	10235,35	304,73	4,85	0,191	53,584	ND	ND	1,224	0,103	0,172	4,515
	5	8,12	18,82	1223,3	15,46	4,31	0,81	21,227	ND	ND	0,971	0,096	0,672	2,757
25/01/18 split sample	1	7,28	0,843	54,79	6,71	NR	0,95	NR	NR	NR	NR	NR	24	NR
	2	8,05	32,2	2093	667,00	NR	<0,1	NR	NR	NR	NR	NR	<0,05	NR
	3	8,76	25,2	1638	513,00	NR	<0,1	NR	NR	NR	NR	NR	<0,05	NR
	4	8,68	11,6	754	227,00	NR	<0,1	NR	NR	NR	NR	NR	<0,05	NR
	5	7,61	0,155	100,75	18,70	NR	0,27	NR	NR	NR	NR	NR	2	NR
28/02/18	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,97	377,82	24558,75	606,35	7,81	0,36	12,82	ND	ND	4,28	0,12	0,38	0,004
	3	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	4	8,84	277,1	18011,76	546,65	3,77	0,23	23,28	ND	ND	4,54	0,12	0,23	0,004
	5	8,3	25,67	1669	112,65	2,06	0,47	19,43	ND	ND	4,43	0,1	0,73	ND
03/03/18	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	3	8,96	388,7	25265,69	257,49	4,04	0,192	18,286	ND	ND	2,105	0,113	0,135	1,814
	4	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	5	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
23/04/18	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	3	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	4	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	5	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
10/05/18 split sample	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	7,94	57,1	3711,5	1430,00	NR	<0,1	NR	NR	NR	NR	NR	0,06	NR
	3	8,93	44,4	2886	1070,00	NR	<0,1	NR	NR	NR	NR	NR	<0,05	NR
	4	8,94	22,2	1443	492,00	NR	<0,1	NR	NR	NR	NR	NR	<0,05	NR
	5	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
06/06/18	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,98	552,31	35900,6	632,31	6,55	0,191	14,4	ND	ND	1,72	0,111	0,18	2,793
	3	9,11	504,08	32765,46	694,08	4,67	0,183	5,864	ND	ND	1,678	0,114	0,158	ND
	4	9,04	496,99	32304,41	857,61	4,67	0,185	6,233	0,022	ND	1,981	0,117	0,172	ND
	5	8,89	79,44	5163,79	278,78	2,33	0,193	18,2	0,056	ND	1,943	0,092	0,136	3,314
11/07/18	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	9,16	557,04	36207,99	566,90	5,83	0,192	14,128	0,007	ND	2,363	0,103	0,138	3,744
	3	9,15	550,89	35808,43	571,57	4,22	0,184	9,923	0,007	ND	2,276	0,116	0,161	ND
	4	9,03	553,73	35992,84	564,82	5,21	0,194	13,019	0,006	ND	2,157	0,119	0,201	2,103
	5	8,68	132,4	8606,32	334,84	3,14	0,196	15,547	ND	ND	1,701	0,1	0,274	3,133
15/08/18	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	3	9,09	622,77	40480,44	603,24	3,59	0,193	11,007	ND	ND	2,044	0,117	0,175	4,485
	4	8,78	154,15	10020,2	316,67	5,92	0,216	16,054	ND	ND	2,296	0,101	0,184	2,007
	5	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
17/09/18	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,85	575,48	37406,72	741,84	5,03	0,196	11,149	0,016	ND	2,575	0,114	0,188	3,779
	3	9,13	597,24	38820,6	724,71	6,55	0,187	6,037	ND	ND	2,371	0,12	0,595	ND
	4	9,03	655,87	42632	799,99	6,46	0,187	7,683	0	ND	2,183	0,11	0,11	ND
	5	8,76	151,79	9866,54	348,34	3,14	0,197	13,038	ND	ND	2,226	0,083	0,039	2,65
08/10/18	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,89	580,69	37744,85	813,49	6,55	0,191	13,663	0,009	ND	2,573	0,083	0,069	4,063
	3	8,93	612,57	40142,31	775,59	5,65	0,186	10,062	0,017	ND	2,875	0,083	0,026	ND
	4	9,1	725,86	47181,03	958,84	5,56	0,186	9,858	0,016	ND	2,313	0,083	0,024	ND
	5	8,7	164,08	10665,65	505,64	3,14	0,217	16,45	ND	ND	74,712	0,096	0,129	4,136
28/11/18	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,8	586,36	38113,66	828,54	13,73	0,222	24,012	ND	ND	1,356	0,114	0,167	5,595
	3	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	4	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	5	8,75	185,36	12048,85	473,97	8,53	0,254	30,941	ND	ND	1,292	0,101	0,216	2,685
11/12/18	1	7,71	13,05	848,31	331,21	3,95	0,501	12,902	0,008	ND	0,718	0,077	0,585	1,464
	2	8,85	467,67	30398,74	636,46	9,33	0,177	6,685	0,089	ND	1,195	0,09	0,067	ND
	3	8,67	162,69	10575,48	306,29	4,22	0,184	13,967	0,011	ND	1,534	0,081	0,072	ND
	4	8,43	63,03	4097,21	129,78	3,95	0,174	7,768	0,011	ND	1,161	0,077	0,078	0,527
	5	6,93	25,77	1675,18	59,18	4,76	0,378	7,229	0,018	ND	1,355	0,076	0,291	ND

DWS Water Quality Guidelines: Green-Target water quality range, Yellow-Tolerable range, Orange-Chronic effect range, Red-Acute effect range.

APPENDIX 2.2

River Water Quality Sampling Results (November 2017 – February 2020) continued

Hg (average)	Ni (average)	Pb (average)	Zn (average)	Sulphates (average)	Chlorides (average)
no flow	no flow	no flow	no flow	no flow	no flow
4.537	0,108	3,336	0,958	107.8	299.55
2.332	0,104	2,229	ND	65.9	164.84
no flow	no flow	no flow	no flow	no flow	no flow
4.322	0,106	0,715	0,047	35.9	49.63
no flow	no flow	no flow	no flow	no flow	no flow
2.425	0,106	2,036	0,03	65.9	131.16
4.709	0,11	2,516	ND	62.9	121.23
4.515	0,108	2,681	ND	59.9	146.76
2.757	0,107	0,423	0,043	35.9	60.61
NR	NR	NR	<0.05	6.46	NR
NR	NR	NR	<0.05	517	NR
NR	NR	NR	<0.05	553	NR
NR	NR	NR	<0.05	213	NR
NR	NR	NR	<0.05	8,34	NR
no flow	no flow	no flow	no flow	no flow	no flow
0,004	NR	7,02	7,02	53.9	306.99
no flow	no flow	no flow	no flow	no flow	no flow
0,004	0,10	6,36	ND	59.9	254.17
ND	0,10	1,89	ND	21.0	30.84
no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow
1,814	0,105	3,34	ND	89.9	356.27
no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow
NR	NR	NR	<0.05	906	NR
NR	NR	NR	<0.05	815	NR
NR	NR	NR	<0.05	384	NR
no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow
2,793	0,105	3,378	ND	77.9	561.17
ND	0,106	3,54	ND	62.9	486.01
ND	0,106	3,517	ND	59.9	487.08
3,314	0,131	1,044	ND	13.2	92.87
no flow	no flow	no flow	no flow	no flow	no flow
3,744	0,137	2,532	0,296	71.9	459.43
ND	0,106	3,871	ND	59.9	442.06
2,103	0,105	4,016	ND	56.9	473.96
3,133	0,107	1,219	ND	11.7	96.42
no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow
4,488	0,107	3,649	0,004	80.9	536.71
2,007	0,104	1,079	0,12	47.9	189.65
no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow
3,779	0,108	3,365	0,017	50.9	531.75
ND	0,105	3,779	ND	NR	85.78
ND	0,16	4,608	ND	NR	645.54
2,65	0,156	1,376	ND	NR	570.39
no flow	no flow	no flow	no flow	no flow	no flow
6,063	0,232	3,472	ND	50.9	529.26
ND	0,27	4,499	ND	63.3	626.4
ND	0,297	5,254	ND	71.9	742.32
4,136	0,172	1,818	ND	ND	82.95
no flow	no flow	no flow	no flow	no flow	no flow
5,595	0,105	3,879	ND	86.9	539.19
no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow
2,685	0,109	1,824	ND	NR	106.7
1,464	0,1	ND	ND	5391.6	35.45
ND	0,099	0,739	ND	68.9	412.63
ND	0,098	ND	ND	19.5	NR
0,037	0,099	ND	ND	NR	72.67
ND	0,224	ND	ND	NR	59.91

APPENDIX 2.3

River Water Quality Sampling Results (November 2017 – February 2020) continued

Date	Site No.	pH	EC(mS/m)	TDS	Na (average)	K(average)	Al (average)	Ca (average)	Cd (average)	Co (average)	Cr (average)
22/01/19	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,73	581,16	37775,59	603,75	13,10	0,201	25,421	ND	ND	1,439
	3	8,36	76,27	4957,87	233,61	3,14	0,18	10,444	0,016	ND	1,813
	4	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	5	8,6	71,35	4638,2	142,24	4,67	0,198	12,452	0,005	ND	1,344
06/02/19	1	7,55	21,23	1380,8	8,13	8,80	0,226	21,228	0,008	ND	1,644
	2	8,64	364,58	23698,09	490,58	6,37	0,191	16,822	0,002	ND	1,121
	3	8,76	410,92	26710,32	750,15	5,83	0,192	14,406	0,007	ND	1,735
	4	8,7	326,28	21208,39	449,57	4,76	0,19	19,489	0,011	ND	1,735
	5	8,25	32,2	2093,19	120,96	3,23	0,203	14,21	0,023	ND	1,762
13/03/19	1	8,45	34,14	2219,23	15,72	1,97	0,19	39,09	0,04	ND	4,4
	2	8,24	88,04	5723,18	124,07	2,24	0,19	67,96	ND	ND	8,75
	3	8,6	115,38	7499,76	195,71	2,78	0,2	53,78	ND	ND	9,12
	4	8,53	114,9	7469,08	165,09	3,68	0,19	54,79	ND	ND	8,34
	5	7,68	18,11	1177,21	71,64	3,14	0,83	14,95	ND	ND	9,02
01/04/19	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	3	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	4	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	5	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
09/05/19	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,63	479,02	31136,43	633,35	7,90	0,2	38,21	ND	ND	8,4
	3	8,47	366,47	23821,07	490,58	3,59	0,2	43,9	ND	ND	7,51
	4	8,43	365,05	23728,83	646,84	3,50	0,2	41,36	ND	ND	9,5
	5	8,12	41,51	2698,67	153,14	3,14	0,2	32,48	ND	ND	8,88
24/06/19	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,54	560,82	36453,88	755,86	7,63	0,19	46,56	ND	ND	8,34
	3	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	4	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	5	8,64	82,65	5372,77	290,72	3,95	0,19	33,43	ND	ND	8,82
04/07/19	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,32	571,23	37130,08	794,80	9,15	0,19	33,43	ND	ND	8,82
	3	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	4	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	5	8,48	124,36	8083,79	199,87	4,04	0,19	33,43	ND	ND	8,82
07/08/19	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,48	593,93	38605,45	857,09	11,22	0,21	88,77	ND	ND	8,74
	3	8,42	473,34	30767,55	592,85	3,68	0,19	36,43	ND	ND	7,96
	4	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	5	8,84	142,33	9251,77	290,20	4,49	0,2	19,56	ND	ND	7,94
10/09/19	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,43	610,95	39712,01	878,38	7,72	0,19	32,12	ND	ND	7,92
	3	8,9	527,72	34302,32	717,45	3,59	0,19	15,65	ND	ND	7,69
	4	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	5	9	163,14	10604,23	342,11	3,23	0,2	11,03	0,06	ND	8,47
08/10/19	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,5	634,59	41248,87	843,59	8,80	0,18	9,5	ND	ND	8,75
	3	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	4	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	5	8,8	192,93	12540,64	375,33	4,04	0,18	9,05	ND	ND	7,8
21/11/19	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,33	500,3	32519,56	642,69	8,53	0,2	125,08	ND	ND	8,69
	3	8,29	409,03	26587,34	555,99	4,13	0,19	50,06	ND	ND	59,6
	4	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	5	7,75	42,55	2766,33	161,45	3,50	0,27	20,28	ND	ND	127,67
18/12/19	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,25	410,45	26679,57	348,34	7,00	0,19	51,21	ND	ND	209,82
	3	8,26	338,1	21976,82	457,36	3,95	0,19	33,57	ND	ND	126,32
	4	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	5	7,58	43,31	2815,47	303,69	3,05	0,38	48,96	ND	ND	156,3
29/01/20	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	7,8	131,45	8544,83	277,74	3,86	0,33	85,19	ND	ND	89,87
	3	7,85	149,42	9712,82	174,95	2,87	0,18	95,39	ND	ND	171,72
	4	7,99	107,34	6977,29	197,27	2,42	0,2	78,75	ND	ND	158,58
	5	8,85	40,4	2626	95,00	2,87	0,21	32,62	ND	ND	105,99
18/02/20	1	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	2	8,01	308	20020	524,85	5,92	0,18	207,22	ND	ND	566,29
	3	8,16	288	18720	486,95	3,50	0,17	473,41	ND	ND	518,56
	4	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
	5	7,42	23,7	1540,5	328,09	2,60	0,41	18,02	ND	ND	154,78

APPENDIX 2.4

River Water Quality Sampling Results (November 2017 – February 2020) continued

(average)	Cr (average)	Cu (average)	Fe (average)	Hg (average)	Ni (average)	Pb (average)	Zn (average)	Sulphates (average)	Chlorides (average)
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	1,439	0,113	0,2	0,862	0,104	1,55	0,206	70,2	515,08
ND	1,813	0,088	0,112	0,378	0,098	ND	0,021	NR	86,85
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	1,344	0,099	0,111	ND	0,099	ND	ND	18,0	65,22
ND	1,644	0,095	0,156	ND	0,096	ND	0,142	20,7	17,72
ND	1,121	0,102	0,119	0,331	0,1	0,106	ND	59,9	342,09
ND	1,735	0,093	0,106	0,411	0,101	0,251	ND	53,9	345,99
ND	1,735	0,09	0,113	ND	0,098	0,078	ND	17,9	54,94
ND	1,762	0,084	0,123	ND	0,098	ND	ND	1347,9	58,13
ND	4,4	0,08	0,07	0,83	0,14	38,54	2,08	6,9	45,02
ND	8,75	0,08	0,08	1,01	0,1	ND	0,1	25,2	NR
ND	9,12	0,09	0,09	1,25	0,11	ND	0,13	28,2	126,55
ND	8,34	0,09	0,08	1,29	0,1	ND	0,18	71,9	115,56
ND	9,02	0,08	1,04	1,21	0,45	ND	0,14	16,5	45,02
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	8,4	0,14	0,1	1,99	0,12	ND	7,57	44,9	432,84
ND	7,51	0,13	0,08	2,03	0,1	ND	1,6	53,9	296,36
ND	9,5	0,13	0,08	1,57	0,1	ND	1,34	47,9	350,95
ND	8,88	0,12	0,08	1,6	0,1	ND	1,22	3294,9	50,33
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	8,34	0,1	0,09	1,66	0,11	ND	0,78	80,9	464,74
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	8,82	0,08	0,07	1,32	0,11	ND	0,82	1347,9	60,61
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	8,82	0,10	0,07	1,32	0,10	ND	ND	83,9	527,85
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	8,82	0,10	0,07	1,32	0,10	ND	ND	17,4	69,48
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	8,74	0,11	0,12	2,15	0,05	ND	2,24	56,9	506,93
ND	7,96	0,1	0,09	2,56	0,03	ND	1,58	62,9	498,78
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	7,94	0,08	0,12	1,89	ND	ND	1,25	2426,2	72,31
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	7,92	0,14	0,09	1,45	0,01	ND	0,76	92,9	567,2
ND	7,69	0,13	0,06	1,57	0,03	ND	0,39	68,9	515,08
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	8,47	0,11	0,07	0,81	ND	ND	0,44	ND	71,6
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	8,75	0,11	0,04	1,82	0	ND	0,03	86,9	598,39
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	7,8	0,1	0,04	1,16	ND	ND	ND	ND	68,06
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	8,69	0,13	0,14	2,94	ND	ND	2,09	77,9	426,81
ND	59,6	0,14	0,07	1,59	0	ND	0,49	44,9	388,53
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	127,67	0,1	0,13	1,53	ND	ND	0,23	17,1	68,06
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	209,82	0,12	0,11	3,22	ND	ND	0,94	43,7	389,95
ND	126,32	0,1	0,07	1,99	ND	ND	0,44	56,9	315,5
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	156,3	0,11	0,34	1,42	ND	ND	0,75	748,8	46,79
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	89,87	0,09	0,44	5,84	0,11	0	1,46	28,2	95,71
ND	171,72	0,11	0,08	1,45	ND	ND	0,75	21,6	136,48
ND	158,58	0,11	0,09	0,13	ND	ND	1,05	18,3	NR
ND	105,99	0,1	0,11	1,97	ND	ND	0,86	11,4	64,51
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	566,29	0,19	0,1	1,79	0,26	4,11	0,65	50,9	268,71
ND	518,56	0,18	0,12	3,17	0,03	ND	0,6	41,9	297,78
no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow	no flow
ND	154,78	0,11	1,16	1,88	ND	ND	0,43	32,9	29,42