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An analysis of the ground water quality within the vicinity of SMC ZIMPLATS mine Tailings dam.

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A dissertation submitted in partial fulfilment of the requirements of a Bachelor of Sciences Honours Degree in Safety Health and Environmental Management.

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DECLARATION

The undersigned certify that they have read and recommended to the Bindura University of Science Education for acceptance of the dissertation entitled "AN ANALYSIS OF THE GROUND WATER QUALITY WITHIN THE VICINITY OF SMC ZIMPLATS MINE TAILINGS DAM".

Submitted by B191383B in partial fulfilment of the requirements of the Bachelor of Science Honours Degree in *Safety Health and Environmental Management.*

Chantelle T. Muzondo		30 / May / 2023
Student	Signature	Date

DEDICATION

To my family.

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I would like to express my sincere gratitude to God for blessing me with the opportunity to undertake this project. I am immensely grateful for waking up every day and providing me with the strength and perseverance to overcome the challenges that came with this project.

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ABSTRACT

The mining sector extracts valuable minerals such gold, nickel and platinum, creating employment to several people and contributing to the success of economies of many countries. However, mining activities present a considerable threat on the environment, through the discharge of pollutants into air, soil and water. Also, tailings dams, which are earthen walls constructed to contain mining wastewater, can contain toxic elements that can easily leach into the ground and contaminate groundwater. As such, the study aimed at evaluating the effects of Selous Metallurgical Complex (SMC) ZIMPLATS tailings dam on groundwater quality. The study employed an experimental design where three replicates of groundwater samples were collected from five random points, making a total of fifteen groundwater samples. Standard methods were then used to analyse the samples for total coliforms, total dissolved solids (TDS), total hardness, pH, nitrates, Cd, Fe and Pb. Results showed that all sampling points contained coliforms ranging from 0.33 to 8.33 CFU/100ml. The TDS in the After mine and Borehole 1 samples were above the WHO permissible limit for drinking water. Total hardness (1886.4 to 2940.9 mg/L) and nitrates (56.9 to 145.7 mg/L) were above the WHO permitted limits across all sampling points. Nitrate were significantly different across sites ($p < 0.05$). pH values were within the WHO threshold (< 7.5), though Borehole 2 was slightly acidic (pH = 5.1±0.01). The Cd concentrations across all sampling sites conformed to the WHO standards as they were below 0.003 mg/L, the Spring (0.27±0.02 mg/L) was the only sampling point to record Fe concentrations within the WHO threshold, whereas the Pb concentrations were above the WHO limit across all sampling points ranging from 0.1±0.0 mg/L (Spring) to 0.05±0.04 mg/L (Borehole 1). The Mine, the After mine and Borehole groundwater samples were not significantly different ($p > 0.05$) in Pb concentrations. Based on these findings, it can be recommended that SMC Zimplats should periodically monitor the groundwater quality so that it complies with the WHO standards. Also, the tailings should be monitored so as to reduce groundwater contamination.

Key words: groundwater, tailings, water quality, and WHO guidelines.

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LIST OF ACRONYMS

AMD	Acid Mine Drainage
ANOVA	Analysis of Variance
Ca	Calcium
Cd	Cadmium
EC	Electrical Conductivity
EDTA	Ethylenediaminetetraacetic acid
Fe	Iron
ICPOES	Inductively Coupled Plasma Optical Electro Spectrophotometry
MDG	Millennium Development Goals
Mg	Magnesium
Pb	Lead
SMC	Selous Metallurgical Complex
SPSS	Statistical Package for Social Sciences
TDS	Total Dissolved Solids
TSF	Tailings Storage Facility
UNICEF	United Nations Children Economic Fund
UV	Ultra Violet
WHO	World Health Organisation
Zn	Zinc

CHAPTER 1: INTRODUCTION AND BACKGROUND

1.1 Introduction

The Zimbabwean economy relies heavily on the mining sector, which extracts valuable minerals such as platinum, copper, and gold. Nonetheless, the mining activities also present a considerable threat on the environment, particularly through the discharge of tailings mining water into the ground. Tailings dams, which are earthen walls constructed to contain mining wastewater, can contain toxic elements that can easily leach into the ground and contaminate the environment and groundwater.

Therefore, the present study seeks to investigate the effect of tailings dams on groundwater quality, and identifying potential sources of pollution. The study will employ various tests and measurements such as pH, coliforms, nitrate, hardness, and other contaminants to determine the quality of groundwater. The findings will inform decisions regarding the safety and remediation of the groundwater. Additionally, the study will highlight its objectives, limitations, and potential beneficiaries.

1.2 Background to the study

A tailings dam is a structure designed to store both tailings and mine water, which can be reused in the mining process (Berkun, 2015). The activities employed during the mining of platinum mining, such as ore extraction and ore processing, produce significant waste quantities. Ore processing involves the physical separation and sorting of the ore as well as chemical treatments. On the other hand, metallurgical involves breaking down crystal bonds that make-up the ore so as to extract the mineral. Unfortunately, these processes result in a large amount of waste, with over 99% of the extracted ore being released into the environment (Minetek, 2022).

According to Minetek (2022), tailings constitute an assortment of liquids and solids, in slurry form which may contain hazardous particles. The tailings sludge, can be used in agriculture, landscaping, and construction industries after removal of toxic elements. Despite the tailings ponds having significant adverse environmental impacts, they are useful in the management of wastewater. Proper management of water tailings can help protect the environment from toxic waste.

Improperly managed water tailings can contaminate groundwater and become a source of ground water pollution, posing significant risks to the environment and human health.

Tailings Storage Facility (TSF) failures can result in dire environmental consequences and even loss of human life (Minetek, 2022). TSF contain hazardous substances that could possibly percolate into groundwater thereby contaminating groundwater and affecting drinking water supplies. Subsequently this could lead to adverse health conditions like carcinogenic effects, gastrointestinal problems, reproductive problems and respiratory concerns. Therefore, proper management of water tailings is crucial.

Tailings refer to the waste material resulting from mineral extraction such as gold, nickel or platinum. As such they typically contain residues of trace elements which can escape into the surrounding environment. These trace elements are not degradable and persist in the environment for several years, affecting the environment and biodiversity. Also, both surface and ground water systems are affected.

According to UNICEF (2011) and WHO (2021), water is a fundamental need for all existing creatures, and has been considered an essential part of achieving the Millennium Development Goals (MDGs). People often only consider groundwater when toxic chemicals have contaminated it, leading to long and challenging journeys to distant water sources (WHO, 2011). However, it is worth noting that globally, half of the water used at household level is groundwater. Also, groundwater constitutes a quarter and a third respectively of irrigation and industrial supplies (WHO, 2011).

This study aims to analyse the heavy metal concentration in groundwater. Heavy metals are prevalent in tailings, which are produced during gold extraction and can leach into the environment, especially groundwater. As heavy metals are non-degradable, their accumulation in groundwater can have significant health and environmental impacts.

1.3 Statement of the problem

Tailings at the Selous Metallurgical Complex (SMC) of ZIMPLATS Mine produce high quantities of hazardous chemicals which leach from the tailings dam and into groundwater and possess the likelihood of adversely impacting human well-being. There are springs near the tailings dam where cattle drink water from and also people use the water for domestic purposes. As such use of the groundwater may lead to clinical effects such as Alzheimer’s disease, behavioural disorders, cardiovascular problems, kidney dysfunction, neurological, and reproductive problems (Luck, 2016). Thus, the level of contamination in the groundwater is worth investigating.

1.4 Justification

The study findings will add literature to the safety and health fraternity, with regards to groundwater quality near tailings dams. The results may provide measurement of success or failure of the tailings dam polluting the groundwater. The study can further be used by other mining organizations as a model or a benchmark. The study can be further used by SMC ZIMPLATS to fill the gap that might exist in the safety, health and environmental system at the tailings dam and help to reduce pollution of ground water if there is any. To the student, the study will help in closing the gap in literature about tailings management and groundwater pollution.

1.5 Aim

To analyse the groundwater quality of water from the springs and hand dug wells near the SMC Tailings dam and evaluate its compliance to Zimbabwe's and WHO drinking water quality standards and guidelines.

1.6 Objectives

1) To determine the pH, total coliforms, total dissolved solids (TDS), total hardness, nitrates and heavy metal concentrations (Cd, Fe and Pb) in groundwater.

2) To compare measured groundwater parameters with WHO drinking water quality guidelines.

1.7 Research Hypothesis

H_o: There is no significant difference in water quality parameters between the groundwater and WHO drinking water quality guidelines.

H1: There is a significant difference between the water quality parameter concentrations in ground water for drinking and WHO drinking water quality guidelines.

1.8 Delimitations

The study is limited to the health and environment part of safety health and environmental management. It will be limited to SMC ZIMPLATS tailings dam thus limited to platinum and gold mine tailings only and also with regards to the geological aspects of the area, as well as concentrations of trace elements in groundwater.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Water is an essential necessity for human survival and opt to be clean and safe, as it acts as a universal solvent with a wide range of applications, including drinking, cooking, industrial processes, and agriculture (WHO, 2021). Failure to treat drinking water to meet the required standards can have adverse health effects and render it unacceptable to end-users. The Alma-Ata International Conference of 1978 identified provision of clean and adequate water supply as a fundamental part of primary health.

Water, being a universal solvent, can transmit various diseases and illnesses if contaminated. Therefore, it is vital to safeguard and enhance the quality of the water supply. In Zimbabwe, water quality has been hampered by several factors leading to poor water and sanitation services in rural and urban areas (Kativhu, 2013). This has resulted in 18% of the population having limited access to safe drinking water, making them susceptible to illnesses and resulting in higher morbidity and mortality rates (Gogo, 2014). In certain African regions, access to clean drinking water is a challenge not due to water scarcity but primarily due to a shortage of safe drinking water (Kaufmann, 2016).

According to Oluyemi *et al.* (2010) water is an essential component of our lives and is used for various purposes, for example, agriculture, domestic, industry, and mining. Contamination of drinking water might result in spread of various diseases hence it is necessary to safeguard and improve water quality. Unfortunately, Zimbabwe still faces poor water and sanitation conditions in rural and urban areas, with several factors compromising the quality of the water supply (Napacho and Manyele, 2010). Shockingly, almost one-fifth of the population lacks access to improved drinking water sources, leading to higher morbidity and mortality rates due to illnesses (Gogo, 2014). In certain African regions, accessing clean drinking water is a challenge not due to water scarcity itself, but primarily due to the scarcity of safe drinking water (Kaufmann, 2016).

2.2 Water from tailings dams

The quality of groundwater near mine tailings dams is a significant environmental concern due to its potential long-term impacts on the environment, human health, and the local economy. Smith (2008) conducted a study on a tailings dam in South Africa and discovered elevated levels of metals in the groundwater, indicating that the tailings dam was a significant source of contamination to the surrounding environment.

Fieseler (2015) analyzed the groundwater quality at a tailings dam in Canada and found contamination with metals and other pollutants, which likely originated from the tailings dam. The study concluded that further remediation was necessary to reduce the environmental and human health risks associated with the tailings dam.

Wang *et al.* (2019) investigated the groundwater quality of a tailings dam in China and determined elevated heavy metal concentrations in the groundwater, signifying that the tailings dam was a probable source of contamination. The authors recommended further monitoring to assess the extent of the contamination and its potential impact on the environment and human health.

2.3 Water treatment

Domestic water can be sourced from underground or surface sources, with groundwater traditionally being considered the safest source of water, particularly in rural communities as noted by Munyebvu (2011). However, due to anthropogenic activities like agriculture and mining, groundwater safety cannot always be guaranteed unless it has undergone necessary treatment measures. Therefore, the most important aspect is water treatment and processing from the source to the end-user.

Water treatment methods vary depending on affordability of the required equipment, infrastructure, and the characteristics of raw water (WCC, 2008). Examples of water purification methods include, boiling, chemical treatment, disinfection, filtration, and sedimentation. SMC ZIMPLATS uses the disinfection method, which involves chlorination to destroy pathogens in water, guarantying safe drinking water and public health protection. However, as Munsaka (2017) points out, mining affects the environment considerably thus the water management and supply system must be advanced. Clean water provision requires science-based solutions, leading to various water treatment methods to address the issue. The appropriate technology for purification depends on factors such as raw water characteristics, affordability/cost, infrastructure, and acceptability, as noted by Sharma and Bhattacharya (2017).

2.4 Water quality

As defined by Gutti *et al.* (2014) water quality refers to the biological, chemical and physical state of water with respect to its use. Thus maintaining its quality is important for public health protection (Oluyemi *et al.*, 2010). The World Health Organisation (WHO) developed water quality standards used as a benchmark for drinking water quality. In addition, these guidelines serve as a basis for monitoring, maintaining and improving water quality (Kativhu, 2013). Considering that drinking water quality varies on a temporal and spatial scale, its assessment should ensure its quality is safe for the end-user (Mugadza *et al.*, 2021).

2.5 Drinking water variables

Daud *et al.* (2017) reported that minor fluctuations in water quality parameters may have significant impacts to human health. Thus, these parameters should be maintained in the ranges as per the regulatory standards. The WHO drinking water guidelines of 2017 specify the required and acceptable thresholds for water quality parameters to enhance water accessibility and prevent jeopardising human health. While many elements are essential at low concentrations, exceeding the recommended levels can make them toxic, according to WHO (2011). Therefore, effective treatment is necessary to prevent public health risks.

Drinking water contains trace elements like Cd, Fe, Pb and Zn, which can pose significant toxicity risks to human health, as highlighted by Xiao *et al.* (2014). As such, the present study intends to evaluate the trace element concentrations in groundwater, with respect to stipulated guidelines. Excess of trace elements has significant adverse health impacts such as cancer, diarrhoea, kidney degradation, cardiovascular and neurological problems (Nzeve, 2015).

2.5.1 Total dissolved solids

Total dissolved solids are inorganic salts and minute quantities of organic matter that are in solution in water (Islam *et al.*, 2017). Theses TDS are mainly composed of anions, bicarbonates, carbonates, chlorides, nitrates and sulphates. Presence of TDS in water is an indication of the existence of other detrimental contaminants. In addition, the TDS affects taste.

2.5.2 Total hardness

According to Sharma and Bhattacharya (2017) water hardness symbolises the presence of Ca or Mg in water. In addition, WHO (2011) asserts that water hardness is the measure of the capacity of water to react with soap, with hard water needing large quantities of soap to produce a lather. Compared with surface water, groundwater possesses high levels of hardness and tis affects its acceptability by consumers.

2.5.3 pH

pH is a measure of acidity or alkalinity whereupon the geology of the catchment area and the buffering capacity of water generally influences water pH (Bajpai, 2012). A lower pH increases the solubility of heavy metals thus affecting water quality.

2.5.4 Nitrates

Presence of nitrates drinking water are a result of contamination with sewage and animal excreta. Consumption of nitrate contaminate drinking water leads to severe adverse health conditions as the nitrates is converted to nitrite in the body. Resultantly it affects transportation of oxygen in the blood leading to respiratory problems (Sharma and Bhattacharya, 2017).

2.5.5 Iron

The importance of water to human health cannot be overstated, and its requirement varies depending on age, sex, and physiological status. Presence of Fe in drinking water is not a health concern, but however, at elevated concentrations, the Fe changes water appearance, making it undesirable for domestic use. In addition, Fe causes an unpleasant, bitter metallic taste (Kusin *et al.,* 2016).

2.5.6 Cadmium

Cadmium is associated with chronic health risks when water is consumed at levels exceeding the maximum acceptable value. Waste water is a major source of Cd contamination in the environment (WHO, 2017).

2.5.7 Lead

According to Sharma and Bhattacharya (2017) elevated concentrations of Pb can cause a range of health effects in humans, such as affecting foetal development, high blood pressure and renal illness in adults. Also, Pb can also replace Ca in bones, especially in pregnant women and infants less than six years old (Ehi-Eromosele and Okieki, 2012).

Table 2.1: WHO 2017 drinking water quality guidelines for selected parameters

Variable	Guideline value (mg/l)	Variable	Guideline value (mg/l)
Cadmium	0.003	pH	6.5- 7.5
Nitrate	50	Total Coliforms	0
Iron	0.3	Total Dissolved Solids	600
Lead	0.01	Total Hardness	1000

2.6 WHO guidelines for drinking water

In Zimbabwe, the standards for drinking water quality are established by the WHO international guidelines, which specify the parameters and maximum allowable levels for each variable. The guidelines also note that certain parameters may not cause clinical effects to humans but can affect water acceptability for domestic use. Some elements are necessary at low concentrations, exceeding the recommended levels can render them toxic, according to WHO (2011). To mitigate health risks for the public, effective treatment is essential to ensure water is safe for domestic use.

CHAPTER 3: METHODOLOGY

3.1 Description of study area

The study was conducted at Selous Metallurgical Complex (SMC), which is under ZIMPLATS Mine, located in Mhondoro, Ngezi, approximately 120 km from Harare, in the Mashonaland Province of Zimbabwe. However, the SMC plant is situated 70 km north of the underground operations and includes a concentrator, smelter, and tailings dam. The mine has been in operation for 40 years, with both open cast and underground mining methods being employed. SMC produces high-quality platinum, gold, palladium, rhodium, ruthenium, iridium, and nickel.

Mhondoro Ngezi has a tropical savannah climate, with an average temperature range of 16°C to 32°C. The region is characterized by sandy loam soil, with some areas containing clay loam. The soil is well-drained and nutrient-rich, making it suitable for growing a variety of crops.

Figure 3.1: Geographic Map of SMC Zimplats Tailings Dam

3.2 Research Design

The study employed an experimental design where water samples were collected randomly in 5 selected sampling sites (Figure 3.2).

Figure 3.2: Sampling Points shown by red dots

3.3 Water samples collection and analysis

Tailings wastewater was collected from five different random sampling points. The sampling points included 1) after the tailings dam, 2) along the springs, 3) within the mining premises, 4) and 5) were selected boreholes near the SMC tailings facility. Grab sampling was conducted, with three replicates collected at each sampling point, using 500ml polyethylene containers that were rinsed three times to prevent contamination of the water samples, as recommended by Triantafyllidou *et al.* (2009). The samples were properly sealed and labelled, stored under 4°C, and transported to the laboratory within 48 hours, following the guidelines outlined by Rice *et al.* (2012). In the laboratory, standard methods of water analysis were performed to evaluate total hardness, nitrates, pH, total dissolved solids, and trace element concentrations.

Table 3.1: Methods used to analyse water parameters

Variable	Procedure
pH	pH and temperature meter
Nitrates	UV Spectrophotometric
Total Hardness	EDTA titrimetric
Total Dissolved Solids	EC and TDS meter
Total Coliforms	Pour plate method
Heavy metals	Inductively coupled plasma atomic emission spectroscopy

NB: Refer to appendices for a detailed explanation of the procedures mentioned in the Table 3.1.

3.4 Quality control procedures

All equipment was calibrated whereas the sampling bottles were initially rinsed inside with deionised water prior to water sample collection. After collection the bottles were then rinsed outside and kept in different compartments to prevent cross-contamination. All analyses were done in triplicate, based on the guidelines provided by the American Public Health Association (1998).

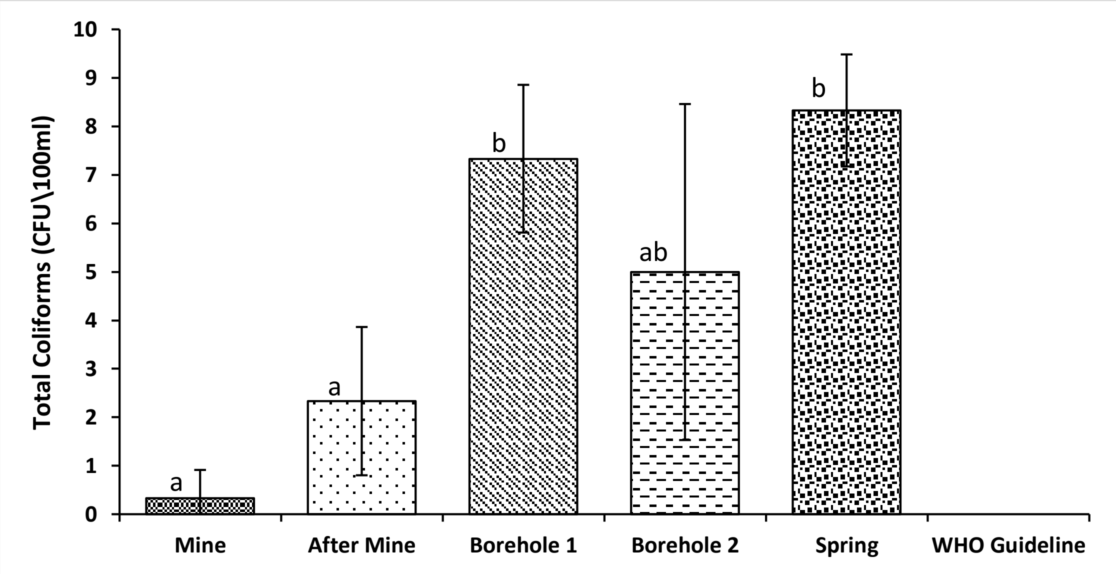
3.5 Statistical Analysis

The data was analysed using the Statistical Package for Social Sciences (SPSS) version 20.0. The mean and standard deviations were calculated. A one-way Analysis of variance (ANOVA) was done to test the significance of difference in the measured water quality parameters between sampling points and with WHO drinking water guidelines. In addition, a 95% confidence level was used and $p < 0.05$ considered statistically significant.

CHAPTER 4: RESULTS

4.1 Total Coliforms

Figure 4.1 shows total coliforms values in groundwater samples from five different sampling points. All sampling points contained coliforms, and were highest in the Spring samples (8.33±1.1 CFU/100ml) and lowest in the Mine samples (0.33±0.5 CFU/100ml). the Mine and After mine samples were not significantly different ($p < 0.05$), whereas the Borehole 1 and Spring samples were also not significantly different ($p < 0.05$).

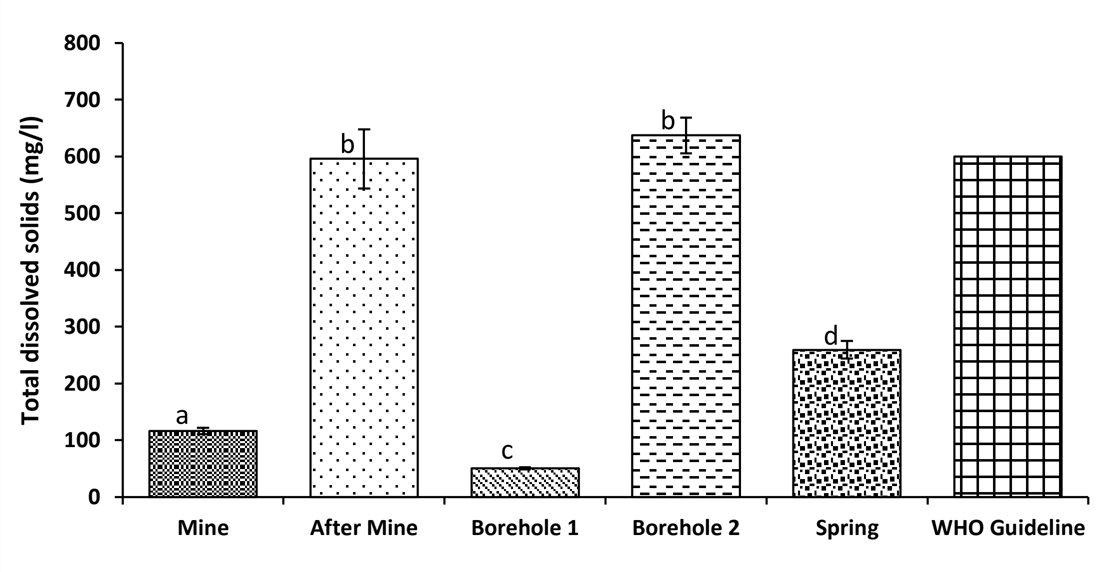


[a, b] superscripts denotes significantly different ($p < 0.05$)

Figure 4.1: Total coliforms in groundwater compared with WHO guidelines

4.2 Total Dissolved Solids

The highest TDS in groundwater were recorded from Borehole 2 (637±31.7 mg/L) whereas the lowest were from Borehole 1 (50.3±1.7 mg/L) (Figure 4.2). The After mine and Borehole 1 samples were above the WHO permissible limit for drinking water. On the other hand, the Mine, Borehole 1 and Spring groundwater samples were within the WHO limits. However, the After mine and Borehole 2 groundwater samples were not significantly different ($p < 0.05$).

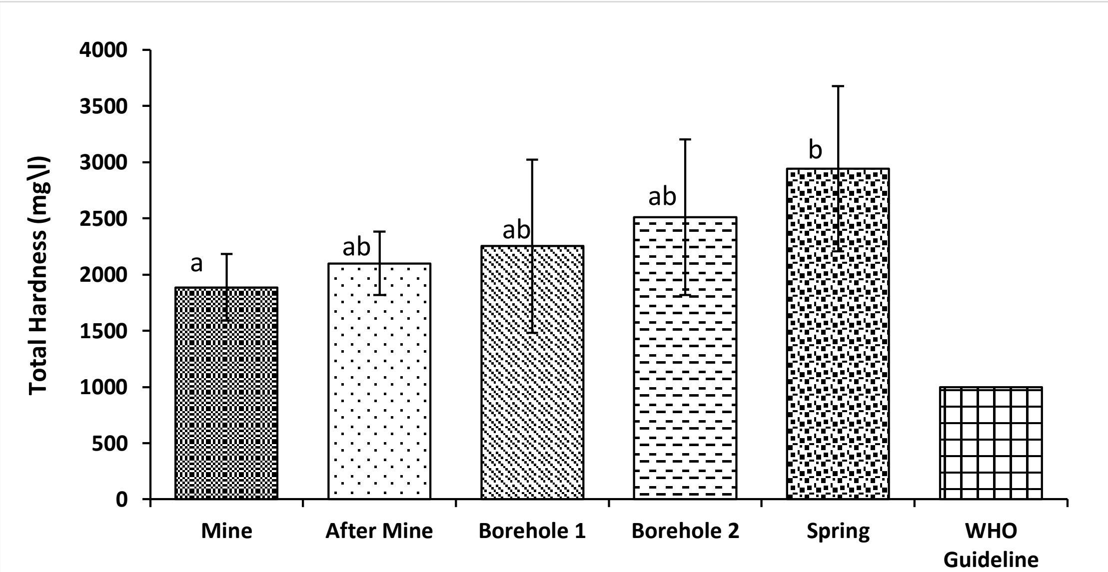


[a, b, c, d] superscripts denotes significantly different ($p < 0.05$)

Figure 4.2: TDS concentration in groundwater compared with WHO guidelines

4.3 Total Hardness

Total hardness across all the sampling points were above the WHO permitted limit of drinking water (Figure 4.3). Total hardness in the Spring samples (2940.9±736.3 mg/L) was almost three times higher than the permissible limit (1000 mg/L). In addition, the Mine and Spring groundwater samples were significantly different ($p < 0.05$).

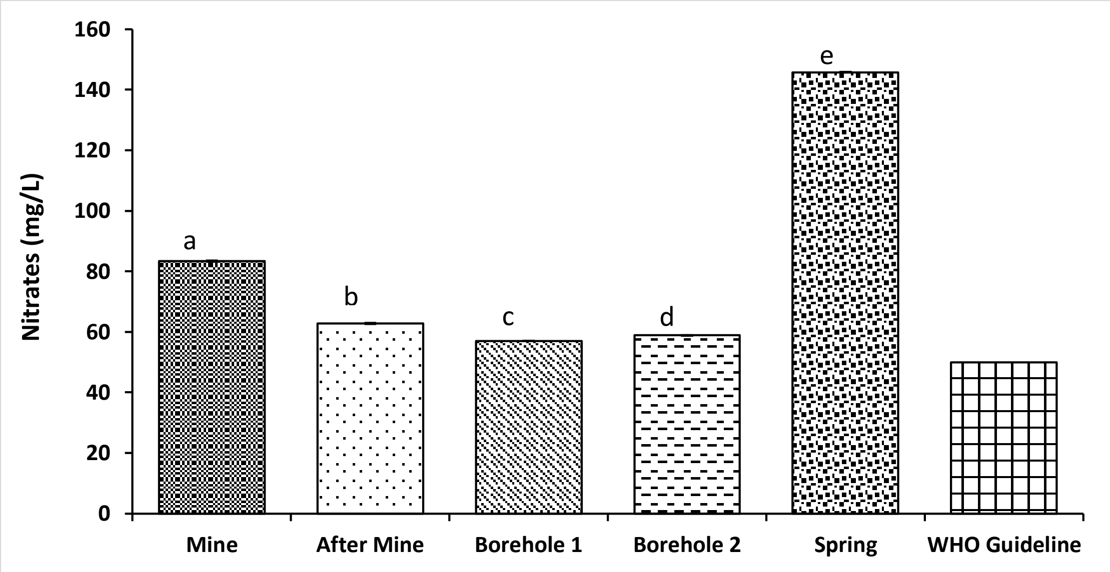


[a, b] superscripts denotes significantly different ($p < 0.05$)

Figure 4.3: Total hardness in groundwater compared with WHO guidelines

4.4 Nitrates

As illustrated in Figure 4.4, nitrate concentrations were significantly highest in the Spring groundwater (145.7±0.1 mg/L) and lowest in Borehole 1 (56.9±0.0 mg/L). Also, all sampling points attained Nitrate concentrations exceeding the WHO permissible limit for drinking water. In addition, nitrate concentrations across sampling points were significantly different ($p < 0.05$).

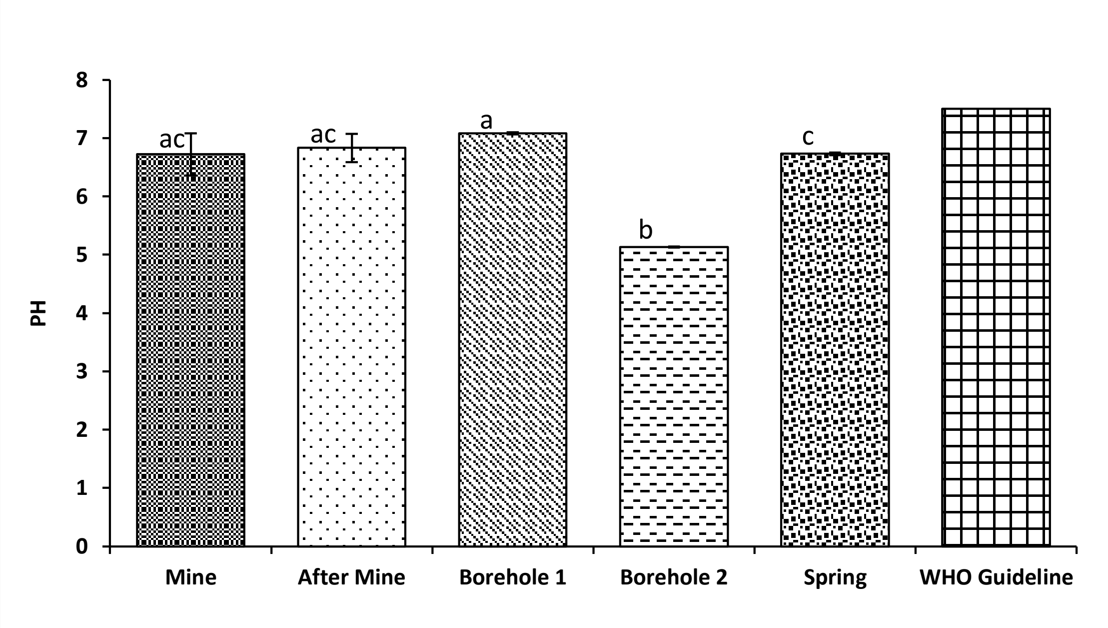


a, b, c, d, e superscripts denotes significantly different ($p < 0.05$)

Figure 4.4 Nitrates concentrations in groundwater compared with WHO guidelines

4.5 pH

Figure 4.5 shows the pH values in groundwater collected from five different points. The pH for all sampling points conformed to the WHO drinking water quality standards. The groundwater pH for the Mine, the After mine, Borehole 1 and the Spring was almost neutral ranging from 6.72 to 7.08. however, Borehole 2 was slightly acidic (pH = 5.1±0.01). In addition, the groundwater from the Mine and the After mine were not significantly different in pH ($p > 0.05$).



a, b, c superscripts denotes significantly different ($p < 0.05$)

Figure 4.5: pH values in groundwater compared with WHO guidelines

4.6 Heavy metal concentrations in groundwater

4.6.1 Cadmium concentrations

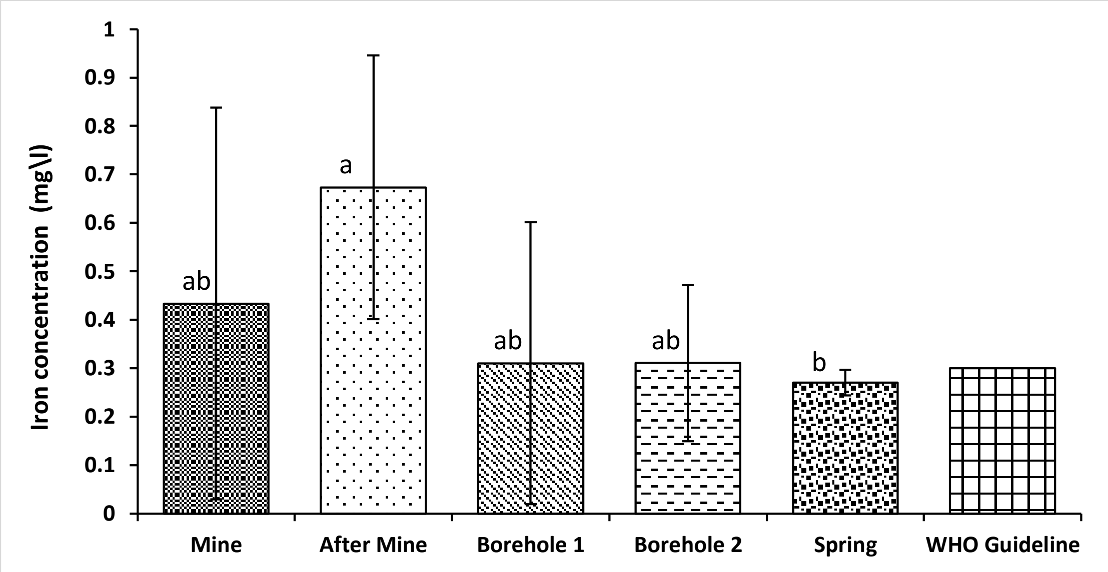
Cadmium concentrations in groundwater are shown in Figure 4.6. The Cd concentrations conformed to the WHO standards of drinking water across all sampling points. The spring (0.001±0.0 mg/L) recorded the significantly lowest Cd value, and was significantly different from other sampling points ($p < 0.05$).

a, b superscripts denotes significantly different ($p < 0.05$)

Figure 4.6: Cadmium concentrations in groundwater compared with WHO guidelines

4.6.2 Iron concentrations

The Spring (0.27±0.02 mg/L) was the only sampling point to record Fe concentrations that were within the WHO drinking water threshold (Figure 4.7). Also, Fe concentrations were significantly highest in the After mine point (0.67±0.27 mg/L). In addition, the After mine and Spring sampling points were significantly different in groundwater Fe concentrations ($p < 0.05$).

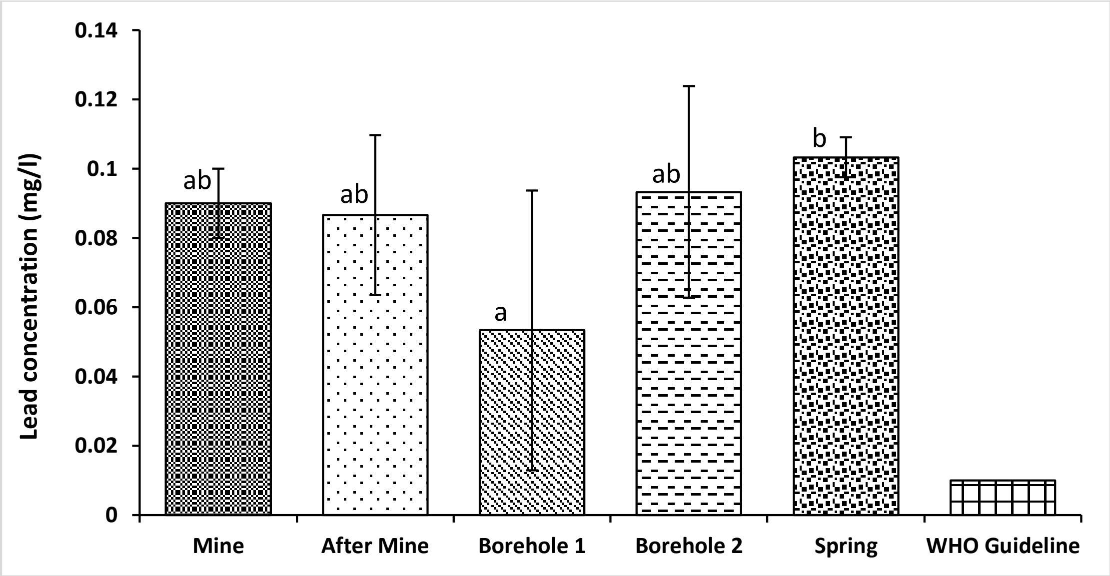


[a, b] superscripts denotes significantly different ($p < 0.05$)

Figure 4.7: Iron concentrations in groundwater compared with WHO guidelines

4.6.3 Lead concentrations

As shown in Figure 4.8 the Pb concentrations were above the WHO drinking water limit across all sampling points. The Spring (0.1±0.0 mg/L) recorded the highest Pb concentrations and Borehole 1 (0.05±0.04 mg/L) the lowest. The Mine, the After mine and Borehole groundwater samples were not significantly different ($p > 0.05$).



[a, b] superscripts denotes significantly different ($p < 0.05$)

Figure 4.8: Lead concentrations in groundwater compared with WHO guidelines

CHAPTER 5: DISCUSSION

5.1 Total coliforms

All sampling points had coliforms detected in the groundwater samples. Such a scenario indicates contamination by faecal matter as such the water is unsuitable for human consumption. Also, the observed high values in the standard error values could have been a result of the higher confidence interval used (95%). In a study by Aram *et al.* (2021) reported 820 CFU/100ml total coliforms that were way above the required limit. Likewise, Apa *et al.* (2019) deduced that total coliform levels were significantly higher in groundwater near the tailings dam compared to groundwater further away from the dam. It was concluded that the tailings dam discharged contaminated water whereas warm temperatures and high nutrient levels yielded such results.

5.2 Total dissolved solids

The TDS can be higher near tailings dams due to the release of dissolved minerals and salts from the waste rock and tailings. These minerals and salts can include sulphates, chlorides, and other inorganic compounds that are present in the ore body. In addition, acid mine drainage can also contribute to the increase in TDS levels, as it can dissolve metals and minerals from the tailings and surrounding rock. The TDS concentration in the present study are lower than those of Acheampong *et al.* (2013) who reported TDS values of 2280±220 mg/L and 2460±92.9 mg/L in process effluent and tailings wastewater respectively.

According to Wang and Mulligan (2009), TDS can be high near tailings dams for several reasons, including *"dissolved metals and metalloids, salts, leaching from the surrounding rocks, evaporation, and discharge from nearby industrial activities"* (p. 231). As Wang and Mulligan explain, tailings dams often contain high concentrations of metals and metalloids, which can dissolve in water and increase the TDS levels. In addition, the salts present in tailings can also contribute to increased TDS levels. Leaching from surrounding rocks and evaporation of water from the tailings dam can further increase TDS levels, and nearby industrial activities may also contribute to elevated TDS levels in the water near tailings dams.

5.3 Total Hardness

Total hardness across all sampling points was high and above the permissible limits, this could be attributed to dissolved minerals, for example Ca and Mg ions released from the tailings. These dissolved minerals can leach into the surrounding soil and water, increasing the hardness of the ground water (Kumar *et al.,* 2017). However, Garba *et al.* (2014) and Huerfano-Moreno *et al.* (2023) reported total hardness within the WHO threshold for drinking water, attaining values of 120.6 mg/L and 9.1 mg/L respectively.

In addition to calcium and magnesium, other dissolved substances such as metal ions and sulphate can also be released from the tailings, contributing to the overall water hardness (Ferreira *et al.,* 2019). Furthermore, the process of acid mine drainage, which occurs when sulphide minerals in the tailings are exposed to air and water, can lead to the release of more dissolved ions into the water, exacerbating the hardness issue (Johnson and Hallberg, 2005).

5.4 Nitrates

Nitrate concentrations were high across all sampling points probably due to the release of nitrogen compounds from the waste rock and tailings. These compounds include ammonium and nitrate, which can be formed during the breakdown of minerals in the tailings. In addition, environmental contamination by nitrates can emanate from the use of explosives in mining operations. However, Acheampong *et al.* (2013) reported low nitrate concentrations in ground water ranging from 3.2 mg/L to 7.6 mg/L.

Nitrates are typically found at higher levels near a tailings dam due to various factors, such as the presence of residual chemicals from the mining process and the decomposition of organic matter (Smith *et al.*, 2020). The tailings dam acts as a storage facility for waste materials generated during the extraction of valuable minerals from ore, which often contain traces of chemicals and heavy metals (Johnson and Jones, 2019). Among these chemicals, nitrogen compounds like ammonium and nitrate are frequently present due to their use in the mining process, such as in explosives or as leaching agents (Brown *et al.*, 2018).

Furthermore, the decomposition of organic matter, such as vegetation and microorganisms, can also contribute to the elevated nitrate levels near a tailings dam (Williams and Garcia, 2021). As organic materials break down, they release nitrogen in the form of ammonium, which can then be converted to nitrate through the process of nitrification by certain bacteria in the environment (Smith *et al.*, 2020). This increase in nitrate can lead to eutrophication and negative impacts on the surrounding ecosystem, including algal blooms and loss of biodiversity (Johnson and Jones, 2019).

5.5 pH

The mean pH for most the samples where within permissible level put in place by WHO expect for sample 4 which was slightly acidic this is because pH range for water near a tailings dam can vary due to factors, such as nature of the mineral ore, the characteristics of the tailings, and the presence of acid mine drainage (AMD). In many cases, tailings contain sulphide minerals, which when exposed to air and water produce sulphuric acid through AMD thus lowering the water pH. Similarly, Acheampong *et al.* (2013) reported a pH value of 7.6±0.4 in tailings wastewater.

According to Wong (2003), tailings with a high buffering capacity can help to neutralize acidic water and resist changes in pH near a tailings dam. Wong explains that when sulphide minerals in tailings are exposed to air and water, they can release H+ ions, which can lower the pH of the surrounding water. However, if the tailings have a high buffering capacity, they can neutralize the H+ ions and maintain a higher pH. That's why sample 4 had a pH that was slightly acidic.

The range of pH near a tailings dam can change over time as the tailings continue to oxidize and release contaminants into the surrounding environment. In addition, the pH range can be influenced by rainfall, temperature, as well as chemicals and minerals in the water. As reported by Cui *et al.* (2016) the water pH was neutral to slightly acidic due to the high buffering capacity of the tailings dam. However, the authors noted that the pH range near the tailings dam could change over time and that monitoring of water quality was necessary to ensure the protection of human health and the environment.

5.6 Heavy metals

Several studies reported the presence of heavy metals in groundwater around mining sites (Acheampong *et al.*, 2013; Patil *et al.*, 2014; Xiao *et al.*, 2017). In the present study, the levels of Cd across all sampling points were lower than the WHO limit (< 0.003 mg/L) this might be because the tailings dam had an effective containment system in place that prevented the release of Cd into the surrounding environment. However, very low standard error values for Cd could signify an insignificant variability in the analysed samples. The tailings dam may have been located far enough away from sources of Cd contamination, such as industrial activities or waste disposal sites, thereby reducing the likelihood of Cd contamination. However, Patil *et al.* (2014) reported high Cd concentrations (> 0.04 mg/L) attributed to pollution from industrial and mining activities. Similarly, Mujere and Isidro (2016) reported higher concentrations of Cd in the upstream area of Revue River that were directly correlated with komatiite, peridotite and serpentine rocks occurring in the area which contained significant Cd concentrations.

The concentrations of Fe observed in this study were higher than the WHO drinking water guidelines (> 0.3 mg/L). also, the large error bards observed for Fe could be attributed to errors in precision of the measuring instrument. The high Fe values correspond with Acheampong *et al.* (2013) and Patil *et al.* (2014) who reported Fe values exceeding 0.9 mg/L and 0.5 mg/L respectively. The Fe content could be resultant of the geology of the study area (Ngezi) which is made up of pyrite parent material derived from the greenstone belt that contains high Fe concentrations. As reported by Hassan *et al.*, (2017), Fe is the mostly found in the form of oxides and hydroxides when its ions (Fe^{2+} and Fe^{3+}) combine with oxygen and compounds containing sulphur. Thus, Fe dissolution will occur due to reduced pH brought about by AMD. As such Fe leaching from the tailings material, and the processes used in mining and mineral extraction led to Fe traces in groundwater. Tailings are waste materials, that can contain elevated concentrations of heavy metals, including Cd, Fe, Pb and Zn (Lottermoser, 2010). Over time, water can infiltrate the tailings material, causing the metals to leach into groundwater (Ritcey, 1989), and is exacerbated by acidic conditions (Johnson and Hallberg, 2005).

The Pb concentrations were high and above the permissible WHO drinking water guideline of 0.01 mg/L. As opined by Hassan *et al.* (2017), bedrock is a source of Fe whereas elements like Cd and Pb emanate from anthropogenic sources. Similarly, Patil *et al.* (2014) reported high traces of Pb ranging from 0.22 mg/L to 0.56 mg/L. In this study, the presence of Pb traces in ground water could be attributed to automobile exhaust, especially leaded gasoline vehicles, oils and vehicle tyres, and lubricant oils which are deposited on to the soil and percolates into the ground thus affecting both soil and groundwater quality. Likewise, Saxena and Saxena (2015) deduced high Pb concentrations in agricultural soils emanating from gasoline deposits proximal to major highways. In addition, the specific processes used in the mining and mineral extraction at SMC Zimplats can also play a role in the high concentrations of heavy metals in groundwater near a tailings dam. For example, the use of chemicals, such as cyanide, in the extraction process can lead to the formation of toxic compounds that can mobilize heavy metals, such as Cd and Pb, in the environment (Lottermoser, 2010).

CHAPTER 6: CONCLUSION AND RECOMMENDATIONS

6.1 Summary

The study investigated the impact of mine tailings wastewater on groundwater quality. Groundwater samples were collected from five sampling points, and analysed for total coliforms, TDS, total hardness, nitrates, pH and selected heavy metals (Cd, Fe and Pb). The concentrations of most of the measured parameters were higher than those stipulated by the WHO drinking water guidelines.

6.2 Conclusion

The analysis of groundwater quality in the vicinity of the tailings dam showed that all sampling points contained coliforms, TDS in the After mine and Borehole 1 samples were above the WHO permissible limit for drinking water. In addition, total hardness (1886.4 to 2940.9 mg/L) and nitrates (56.9 to 145.7 mg/L) were above the WHO permitted limits across all sampling points, and the pH values were within the WHO threshold (< 7.5). Cd concentrations across all sampling sites conformed to the WHO standards as they were below 0.003 mg/L, whereas the he Spring (0.27±0.02 mg/L) was the only sampling point to record Fe concentrations within the WHO threshold. Also, Pb concentrations were above the WHO limit of 0.01 mg/L. This indicates that the groundwater in this area has been impacted by the operations of the nearby tailings dam and may not be suitable for drinking or other domestic purposes without proper treatment.

6.3 Recommendations

It is recommended further long-term monitoring of the groundwater quality, especially the heavy metal concentrations, should be conducted to assess trends over time. If concentrations are found to be increasing, mitigation measures may need to be taken. Some of the mitigation measures include. Liner systems: Installing impermeable liner systems such as geo-membranes below and around the tailings dam to prevent seepage of contaminants into groundwater. These need to be properly installed and monitored regularly for any punctures or tears. Slurry walls: Constructing low permeability slurry walls around the perimeter of the tailings dam to limit transport of contaminants beyond the walls. These walls need to extend deep enough to penetrate low permeability layers.

Cut-off walls: Installing vertical cut-off walls such as sheet piles or cement-bentonite walls around the dam. These walls create a barrier and direct the seepage towards a collection system. Seepage collection: Installing drainage collection systems such as French drains or drainage trenches around the dam to collect any seepage and transport it to a wastewater treatment facility. This prevents uncontrolled release of contaminants into groundwater.

SMC Zimplats should employ treatment technologies like ion exchange and reverse osmosis, could be explored to treat the groundwater if the quality concerns persist or worsen over time before the water is used for any purpose. This will help promote the quality of the water before residents can use it. Best practices should be adopted for management of tailings including erosion control, dust control, proper closure and reclamation of unused parts of the tailings storage facility to minimize infiltration of contaminants into the groundwater.

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APPENDICES

Appendix 1: Mcconkey pour plate procedure for total coliforms

Materials and Equipment needed:

- MacConkey Agar medium
- Sterile Petri dishes (90-100mm)
- Sterile pipettes (1 mL or 10 mL)
- Sample to be tested water)
- Sterile graduated cylinder
- Sterile test tubes or bottles
- Sterile dilution blanks (Buffered Peptone Water, Phosphate Buffer, or equivalent)
- Incubator (35-37°C)
- Bunsen burner or laminar flow hood (for aseptic technique)
- Colony counter or stereoscope

Procedure:

- Preparation of dilutions:

A series of dilutions of the sample were prepared using a sterile dilution blank called Phosphate Buffer.

- Preparation of MacConkey Agar medium:

MacConkey Agar medium was prepared as per the instructions of the manufacturer and autoclaved at 121°C for 15 minutes. The medium was allowed to cool to approximately 45-50°C before being used.

- Pour plate technique:

Under aseptic conditions, a known volume of 1ml was pippeted of each dilution onto the centre of a sterile Petri dish.15-20 mL of molten MacConkey Agar (cooled to 45-50°C) was gently poured onto the Petri dish containing the sample. The dish was gently swirled to mix the sample evenly with the agar.

- The agar was allowed to solidify at room temperature.

Figure 1a: Solidifying petri dishes

- Incubation:

The Petri dishes were inverted and incubated at 35-37°C for 48 hours.

- Enumeration of colonies:

After incubation, the plates were examined for typical coliform colonies. On MacConkey Agar, coliforms appeared as pink to dark red colonies surrounded by a pinkish-purple zone due to the fermentation of lactose. The number of coliform colonies on plates was counted with 30-300 colonies (considered countable) the total coliforms were calculated per mL or gram of the original sample.

Appendix 2: Total Dissolved Solids (TDS) Analysis

Materials used

- EC/TDS meter from Bante instruments 530.
- Distilled water.
- Calibration solutions.
- 5- 500ml beakers.

Figure 2a: EC/TDS meter used.

Procedure

- Distilled water was used to rinse the beakers first.
- Sample mixing was done in the 500ml beaker.
- A 100ml sample was extracted from each sampling bottle.
- Concentration standards of 14.3 ms/cm, 12.88 ms/cm and 111.8 ms/cm of Potassium Chloride were used to calibrate the EC/TDS meter.
- Sample analysis was done by dipping the EC/TDS meter probe in the homogeneous sample.
- To avoid cross contamination in-between switching of the probe from one sample to another sample, the probe was rinsed using distilled water.

Appendix 3: Total Hardness, EDTA Titrimetric method

Materials needed:

- 0.01M of Ethylenediaminetetraacetic acid (EDTA) solution was prepared by dissolving 3.723g of EDTA disodium salt in distilled water and diluted to 1 litre.
- Eriochrome Black T indicator: It is a metallochromic indicator that changes colour based on the presence of metal ions like calcium and magnesium.
- Buffer solution: Ammonia-ammonium chloride buffer is used to maintain pH between 10-11 during titration.
- Distilled water: To prepare solutions and for rinsing apparatus.
- Burette: To deliver EDTA titrant.
- Pipette: To measure sample volume.
- Conical flask: To contain the sample during titration.

Figure 3a: Titration

Procedure:

- 50 ml of the water sample was pipetted into the conical flask.
- 1-2 ml of Eriochrome Black T indicator and 2-3 ml of buffer solution were added, turning the solution into a wine red colour.
- Standard 0.01M EDTA was filled into the burette and an initial burette reading was recorded.
- The water sample was titrated with EDTA solution. The flask was swirled after each addition of titrant.
- Near the endpoint, the colour changed from wine red to blue. The titrant was added dropwise until the solution turned from red to blue.
- The final burette reading was noted. The difference between the final and initial readings gave the volume of EDTA used.
- 1 ml of 0.01M EDTA solution reacted with 1 mg of calcium carbonate ($CaCO_3$) hardness. So, EDTA volume used x 10 = Total hardness as mg/L $CaCO_3$.
- The hardness of the sample in mg/L $CaCO_3$ is = $\frac{a}{b} * 1000 * 10$

Appendix 4: UV Spectrophotometric procedure for Nitrates

Materials needed:

- Nitrate standard solutions: Solutions of known nitrate concentrations like 10, 20, 30 mg/L were used to prepare a calibration curve
- Cadmium reduction column: it reduces nitrates to nitrites. The sample was passed through this column before analysis.
- NEDD reagent: N-1-naphthylethylenediamine dihydrochloride. It reacts with nitrites to form a reddish compound that absorbs at 520 nm.
- Distilled water: For reagent preparation and making standard solutions.
- Spectrophotometer: To measure absorbance at 520 nm.
- Cuvette: For holding the prepared sample solution during absorbance measurement
- Volumetric flask: For making standard solutions and nessler reagent.

Procedure:

- NEDD reagent was prepared by dissolving 1.6 g NEDD in 1 L distilled water containing 4 g NaCl and stored in an amber bottle.
- 100 ml of the water sample was passed through the cadmium reduction column at the rate of 5 ml/min to reduce nitrates to nitrites, the sample was collected.
- Calibration standards of 10, 20 and 30 mg/L Nitrate-N was prepared from the stock standard of 100 mg/L Nitrate-N. Absorbance was measured of each sample at 520 nm.
- A reduced sample and standards of 1ml each were pippeted into 25 ml volumetric flasks.
- 1 ml NEDD reagent was added to each flask and made up to 25 ml with distilled water. This was then mixed well and let stand for 20 minutes.
- The absorbance of the prepared samples and standards at 520 nm was measured using the spectrophotometer and distilled water as blank.
- Through plotting absorbance against concentration of the standard solutions, a calibration curve was prepared and used to determine the concentration of nitrates in the water sample.
- Nitrate concentration (mg/L) = $\frac{Reading\ from\ graph * 100}{Sample\ volume\ passed\ through\ column\ (ml)}$

Appendix 5: Material and Methodology used for pH Analysis

Materials used

- pH meter.
- 5* 500ml beakers.
- Distilled water.

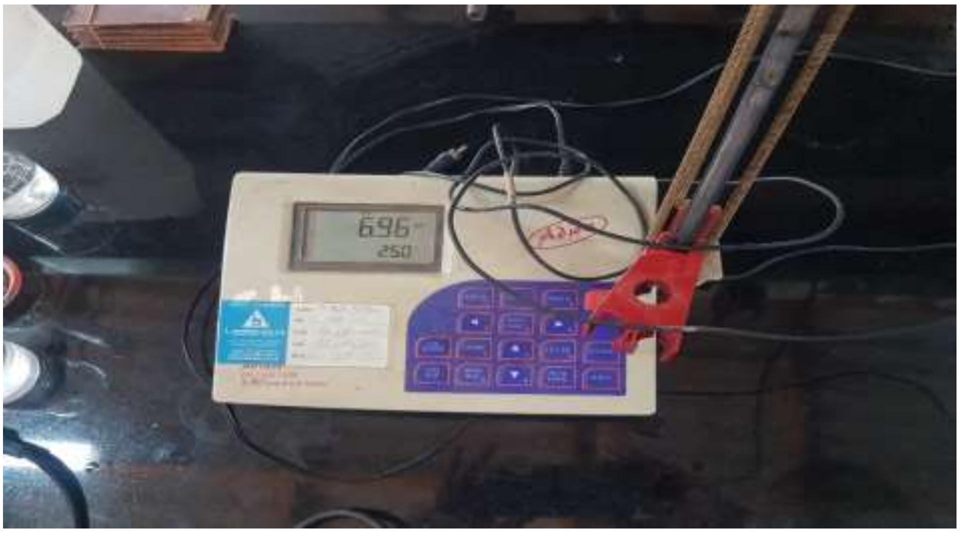

Figure 5a: Picture of a pH meter used

Procedure

- 100 ml from each sampling of water (5 bottles) from each sampling site was extracted and added to the 500ml beaker.
- The beakers were washed using distilled water to remove contamination.
- The pH meter was calibrated using 4 (acidic),7 (neutral) and 9 (alkaline) buffer solutions to cover the range of the p H meter.
- pH meter calibration was tested using distilled water.
- To determine the pH of the water samples, the pH meter probe was dipped in the prepared 5 samples and a reading was taken.
- To avoid cross contamination in-between the switching from one sample to a different sample the pH probe was rinsed using distilled water.

Appendix 6: Materials and Methodology used for metal analysis

Materials used

- 5 * 500ml beakers.
- Inductively coupled plasma atomic emission spectroscopy (ICPOS).
- Distilled water.
- 15 cuvettes.

Methodology

- The beakers were washed with distilled water before use.
- The samples were mixed in the beakers to ensure uniformity.
- 100ml of sample was taken from each of the 5 sample bottles, resulting in a total of 500ml of homogeneous sample for each borehole.
- The homogeneous samples were poured into cuvettes for analysis.
- Each borehole had three homogeneous samples, resulting in a total of 15 cuvettes for all five boreholes.
- To create a calibration curve, the ICPOES was calibrated using concentrations ranging from 1ppm to 5ppm.
- The ICPOS was then used to analyse the samples.

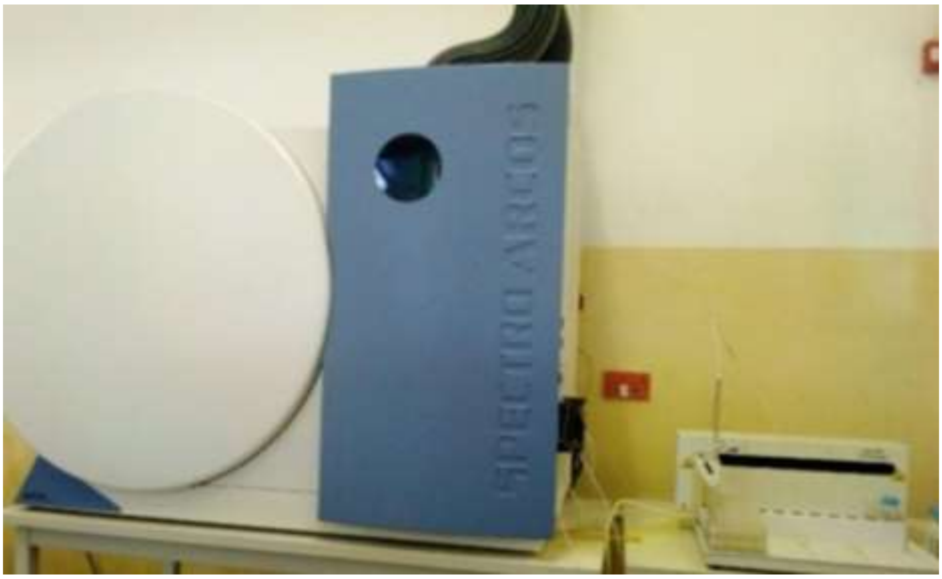

Figure 6a: Picture of ICPOES used

Appendix 7: SPSS Output

Variable	Sample location	Replicates	Mean	Std. dev.	Std. error	Mean difference	95% confidence level	
							Lower bound	Upper bound
Total coliforms	Mine	3	0.3333	.57735	.33333	.33333	-1.1009	1.7676
	Aftermine	3	2.3333	1.52753	.88192	2.33333	-1.4612	6.1279
	Borehole 1	3	7.3333	1.52753	.88192	7.33333	3.5388	11.1279
	Borehole 2	3	5.0000	3.46410	2.00000	5.00000	-3.6053	13.6053
	Spring	3	8.3333	1.15470	.66667	8.33333	5.4649	11.2018
Total dissolved solids	Mine	3	50.2667	1.67432	.96667	-483.66667	-497.3482	-469.9851
	Aftermine	3	116.3333	5.50757	3.17980	-4.33333	-134.4209	125.7542
	Borehole 1	3	637.0000	31.76476	18.33939	-549.73333	-553.8926	-545.5741
	Borehole 2	3	259.3333	15.50269	8.95048	37.00000	-41.9080	115.9080
	Spring	3	595.6667	52.36729	30.23427	-340.66667	-379.1775	-302.1559
Total hardness	Mine	3	1886.0000	296.99663	171.47109	886.00000	148.2195	1623.7805
	Aftermine	3	2100.6667	283.05712	163.42310	1100.66667	397.5138	1803.8195
	Borehole 1	3	2252.6667	770.94769	445.10685	1252.66667	-662.4736	3167.8069
	Borehole 2	3	2510.0000	690.62218	398.73090	1510.00000	-205.6006	3225.6006
	Spring	3	2940.6667	736.01721	424.93973	1940.66667	112.2986	3769.0348
Nitrates	Mine	3	83.3400	.21000	.12124	33.34000	32.8183	33.8617
	Aftermine	3	62.8200	.21000	.12124	12.82000	12.2983	13.3417
	Borehole 1	3	56.9000	.00000a	.00000	13.9000	13.9994	14.000
	Borehole 2	3	58.9400	.12124	.07000	8.94000	8.6388	9.2412
	Spring	3	145.7667	.11547	.06667	95.76667	95.4798	96.0535
pH	Mine	3	6.7333	.37528	.21667	-.26667	-1.1989	.6656
	Aftermine	3	6.8300	.24269	.14012	-.17000	-.7729	.4329
	Borehole 1	3	7.0800	.02000	.01155	.08000	.0303	.1297
	Borehole 2	3	5.1333	.01155	.00667	-1.86667	-1.8954	-1.8380
	Spring	3	6.7300	.02646	.01528	-.27000	-.3357	-.2043

Cadmium	Mine	3	0.002	0.0028	0.0016	0.0006	-.044347687	.0116867
	Aftermine	3	0.002	0.0028	0.0016	0.0006	-.044347687	.0116867
	Borehole 1	3	0.002	0.0028	0.0016	0.0006	-.044347687	.0116867
	Borehole 2	3	0.002	0.0028	0.0016	0.0006	-.044347687	.0116867
	Spring	3	0.001	0.0014	0.0008	0.0003	-.221738435	0.0584335
Iron	Mine	3	0.4334	0.6127	0.3537	0.1444	-.034557932	.129083099
	Aftermine	3	1.6333	1.3054	0.7536	0.5444	.028010988	.124547850
	Borehole 1	3	1.4266	1.2102	0.6987	0.4750	.001020718	.010299742
	Borehole 2	3	0.3836	1.0019	0.5784	0.1270	.005140934	.008010642
	Spring	3	1.1033	0.3618	0.2088	0.3677	.002424113	.005228603
Lead	Mine	3	0.2166	0.0378	0.0218	0.0722	-.070425562	.247955832
	Aftermine	3	0.0866	0.1226	0.0707	0.0288	.096797990	0.366642119
	Borehole 1	3	0.2300	0.04243	0.0244	0.0141	1.554757580	0.9697780420
	Borehole 2	3	0.1233	0.1744	0.1006	0.0411	0.173561593	1. 67543239
	Spring	3	0.1066	0.5555	0.3204	0.0355	0.862987333	0.95678432