SPECIATION ANALYSIS OF CHROMIUM IN NATURAL WATER

By

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DECLARATION

I, **Thenga Dembe [16014370]** declare that 'Speciation analysis of chromium in natural water is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution. All the sources used or quoted have been indicated and acknowledged by means of complete reference.

Signed (Student): ... . **Date: 25.02.2025**

Thenga Dembe

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All the glory and honour to the almighty God for granting me strength and knowledge throughout my studies.

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Plagiarism declaration

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ABSTRACT

Individuals residing in the vicinity face potential exposure to detrimental substances that could be present in the water from rivers and dams. Water pollution is a serious problem that the world is facing. Exposure to water pollution or contamination can occur through ingestion; drinking contaminated water; or the direct consumption of polluted water from taps, wells, rivers, dams, or other sources, which end up impacting human health and the environment. Determining the amount of chromium species present in water samples is therefore essential.

The purpose of this research was to speciate analysis of chromium in natural water samples obtained from the Dzindi river, Mutale river, Luvuvhu river, and Nandoni dam in the Limpopo province using atomic absorption spectrometry. Speciation is the study of an element's chemical forms in a sample, revealing diverse bio availabilities, toxicities, and behaviours. Total chromium, trivalent chromium, and hexavalent chromium are the main species of interest. Chromium in natural water is crucial due to its environmental and human health impacts. In trace amounts, Cr^{3+} is necessary, but Cr^{6+} is highly toxic and carcinogenic, endangering ecosystems and human health. The high solubility and mobility of Cr^{6+} in water, which raises the possibility of it contaminating drinking water sources and being absorbed by living things, led to the identification of this species as the most toxic one in this study. After long-term exposure, Cr^{6+} can result in serious health problems such as liver damage, lung cancer, and other conditions. This study's speciation approach comprised collecting water samples and separating and quantifying Cr^{3+} and Cr^{6+} using methods including inductively coupled plasma optical emission spectrometry and flame atomic absorption spectroscopy.

The instruments that were used in this study, inductively coupled plasma optical emission spectrometry, are particularly useful for chromium speciation due to their ability to accurately detect and quantify the total amount of chromium. Flame atomic absorption spectroscopy is employed in the analysis of total chromium and the hexavalent chromium concentration.

Then the samples were additionally examined for physicochemical parameters: pH, temperature, electrical conductivity, and total dissolved solids. The World Health Organization (2008), SANS

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241 (2006), and Canadian Guidelines (2007) were employed as benchmarks for water quality for drinking reasons. Results indicate that water samples from Nandoni dam exhibited elevated physicochemical parameters, including total dissolved solids and electrical conductivity, throughout the dry and rainy seasons. The quantification of Cr by inductively coupled plasma optical emission spectrometry revealed increased concentrations during the rainy season compared to the dry season. The chromium values during the dry season ranged from 2.607 ± 0.134 mg/L - 4.613 ± 0.236 mg/L; during the rainy season, they ranged from 3.687 ± 0.174 – 6.803 ± 0.462 mg/L.

The water samples were analysed for the total Cr and Cr (VI) concentrations using flame atomic absorption spectroscopy. The total concentrations of chromium in the water of the Dzindi river during the dry season were measured to be 2.406 ± 0.105 µg/L, while during the rainy season, they were found to be 3.651 ± 0.204 µg/L. Similarly, in Mutale River, the concentrations during the dry season were 3.531 ± 0.324 µg/L; during the rainy season, they were 4.401 ± 0.073 µg/L. In Luvuvhu river, the concentrations during the dry season were 2.803 ± 0.215 µg/L; during the rainy season, they were 5.013 ± 0.342 µg/L. Finally, in Nandoni Dam, the concentrations during the dry season were 4.245 ± 0.402 µg/L; during the rainy season, they were 6.304 ± 0.431 µg/L.

After conducting speciation analysis using flame atomic absorption spectroscopy, it was observed that hexavalent chromium's content was significantly high than trivalent chromium. The results of Cr (VI) in the Dzindi river during the dry season were 1.501 ± 0.092 µg/L, while during the rainy season, it was found to be 2.134 ± 0.143 µg/L. Similarly, values in the Mutale river were 2.021 ± 0.057 µg/L during the dry season and 3.704 ± 0.171 µg/L during the rainy season. In the Luvuvhu river, the values were 1.704 ± 0.142 µg/L in the dry season and 3.501 ± 0.184 µg/L in the rainy season. In conclusion, the values at Nandoni dam were 5.819 ± 0.158 µg/L during the rainy season and 3.434 ± 0.138 µg/L during the dry season. As the concentration of Cr (III) were found to be 0.905 ± 0.013 µg/L during dry season and 1.517 ± 0.061 µg/L during rainy season in Dzindi river, Mutale river were 1.510 ± 0.0267 µg/L during the dry season and 0.697 ± 0.098 µg/L during the rainy season. In the Luvuvhu river, the values were 1.009 ± 0.073 µg/L in the dry season and 1.512 ± 0.158 µg/L in the rainy season. Lastly, the values at Nandoni dam were 0.811 ± 0.264 µg/L during the rainy season and 0.485 ± 0.273 µg/L during the dry season as it was calculated the

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difference between the concentration of total chromium and Cr (VI). Based on the data collected from all sample sites (Dzindi river, Mutale river, Luvuvhu river, and Nandoni dam), it can be inferred that the concentration of Cr is within the World Health Organization (2017) and South African Standard guidelines (2005), even though the water contains more Cr (VI) than Cr (III), therefore it is suitable for domestic uses.

Regularly monitoring chromium levels in water from all sampling locations is necessary to accurately determine the concentrations of different chromium species, especially the hazardous Chromium (VI) species, as it causes lung cancer. Examining seasonal variations can be accomplished across all the seasons. The municipality must enhance community awareness and educate residents about the impacts of water contamination.

Key words: Chromium speciation, Water, Chromium pollution, ICP-OES, FAAS, and Nandoni dam, Luvuvhu river, Dzindi river, Mutale river.

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ABBREVIATIONS AND ACRONYMS

ATSDR	Agency for Toxic Substances and Disease Registry
AAS	Atomic absorption spectrometry
DWAF	Department of Water Affairs and Forestry
FAAS	flame atomic absorption spectrometry.
EC	Electrical conductivity
GFAAS	Graphite furnace atomic absorption spectrometry
HGAAS	Hydride Generation Atomic Absorption Spectrometry
ICP-AES	Inductively coupled plasma atomic emission spectrometry
ICP-OES	Inductively coupled plasma–optical emission spectrometry
ICP-MS	Inductively coupled plasma-mass spectrometry
LOD	Limit of detection
MCL	Maximum contaminated level
Ppb	Part per billion
PSS	Proximal soil sensing
SABS	South African Brewer Services
SANS	South African National Standards
SPE	Solid phase extraction
SPME	Solid phase micro extraction
TDS	Total dissolved solid
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

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CHAPTER 1: INTRODUCTION

This chapter provides preliminary background and speciation of chromium. It also gives problem statement and motivation of the study. These sections also include the main objectives and objectives.

1.1 Background

According to Calisevic et al. (2009), South Africa is well known for having a shortage of water. As a result, residents are compelled to use untreated water from rivers and dams for domestic tasks, irrigation, and other agricultural activities. Therefore, the water they are relying on is polluted, as river and dam water is likely contaminated with trace metals such as chromium (Cr) (Varol, 2011). Surface and groundwater bodies can often get contaminated with Cr due to both natural and man-made sources. Cr is thought to be hazardous as it results in lung cancer, kidney failure, asthma, and other health problems like ulcers and diarrhoea. The permissible limit for Cr is 0.05 mg/l (50 µg/l) (WHO, 2017).

The study by Edokpayi et al. (2014) investigated trace metal contamination in Mvudi river water from January to June 2014 using inductively coupled plasma mass spectrometry (ICP-MS). Monthly average concentrations (in mg/L) were found to vary as follows: Aluminium (Al) (1.10–9.644 mg/L), Cadmium (Cd) (0.0003-0.002 mg/L), Chromium (Cr) (0.015–0.357 mg/L), Copper (Cu) (0.024-0.185 mg/L), Iron (Fe) (0.702–2.645 mg/L), Manganese (Mn) (0.018–0.521 mg/L), Lead (Pb) (0.002-0.042 mg/L), and Zinc (Zn) (0.031–0.261 mg/L). In a study by Hemmatkhah et al. (2009), using flame atomic spectrometry and dispersive liquid-liquid microextraction, Cr speciation in rivers revealed concentrations ranging from 7.0 ± 0.18 (Cr (III)) to 7.45 ± 0.25 (Cr (VI)). Sea water samples showed concentrations of 2.31 ± 0.16 (Cr (III)), with no detection of Cr (VI) or Cr (III) in tap water.

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In the earth's crust, Cr is found naturally. Although chromium can be found in a variety of oxidation states, from 0 to VI, only Cr (III) and Cr (VI) are frequently found in the environment. The principal source of chromium is soil, which is the ambient state of Cr (III) and Cr (VI). Hexavalent chromium is mostly found in anoxic conditions, and trivalent chromium is mostly found in anoxic conditions. Trivalent chromium (Cr III) is an essential nutrient. Trivalent Chromium Cr (III) supplements are commonly utilized to develop muscle or cause weight loss (Levina and Lay, 2008). Hexavalent Cr (IV) is toxic, carcinogenic, and causes lung congestion, vomiting, and severe diarrhoea (Das and Mishra, 2008). Hexavalent chromium (Cr (VI)) readily infiltrates the cell membrane and propagates its detrimental effects within the cell, leading to the development of cancer.

The most commonly used methods for speciation of Cr have been atomic spectrometric methods such as ICP-MS, FAAS, graphite furnace-atomic absorption spectrometry (GF-AAS), or inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Xiao et al., 2013). ICP-AES is a widely recognized method characterized by its quick sample analysis, low detection limits, and high sensitivity. In situations where more precise measurements are needed, inductively coupled plasma mass spectrometry is employed. The present investigation used FAAS to measure Cr (VI) and total Cr concentrations in water. This is because of its demonstrated dependability, low sample utilization, great adaptability from interferences, low running costs, excellent detection limits, and ease of handling with full automation. According to Garcia and Baez (2012), FAAS typically has detection ranges between 1 and 100 µg/L, which makes it an ideal instrument for determining the presence of Cr in naturally polluted water samples.

In this project, speciation analysis of chromium in natural water samples from four different sampling locations (Dzindi river, Luvuvhu river, Mutale river, and Nandoni dam) in Limpopo Province, South Africa, was performed. FAAS was used in this current study for the speciation of chromium in natural water samples.

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1.1.1 Chromium speciation

Chromium speciation has become an important study of the environment due to its different toxicity and chemical properties. Because chromium is widely used in many industrial processes, such as tanning, electroplating, pigment manufacturing, and wood preservation, chromium speciation has been a crucial historical endeavour. Large amounts of chromium compounds are discharged into our environment as a result of these industrial operations, which may have an effect on the ecology and biology of the ecosystem. Therefore, the assessment of chromium speciation is essential in order to ascertain the degree of contamination. Beyond its toxicity, chromium speciation affects its mobility as well. Therefore, in order to properly assess the physiological and toxicological impacts of chromium, as well as its chemical change in water, soil, and transport in the environment, a thorough understanding of each species of chromium rather than the total level of Cr is necessary (Bobrowski et al., 2004; El-Shahawi et al., 2005).

Chromium-Cr speciation has received much attention, in relation to drinking water. World Health Organization's (WHO) maximum permissible amount of chromium in drinking water (50 μg/L) is a major contributing factor to this, even though its effects on health are well-established (WHO, 2017). The highest levels of the Cr species that are allowed in wastewater, however, are 1 mg/L for Cr (III) and 0.1 mg/L for Cr (VI) (WHO, 2003). Because the Mutale river, Dzindi river, Luvuvhu river, and Nandoni dam provide water for local inhabitants' household and agricultural needs, it is crucial to investigate Cr speciation in natural water obtained from these sources. Revealing Cr species in natural water is also necessary to comply with regulatory standards. According to Miguel et al. (2015), the total concentration of Cr in groundwater is low (< 1 μg/L), while the dissolved Cr content is between 0.02 and 0.3 μg/L in surface water. Experts recommend quantification levels in the sub-mg/L range for hexavalent Cr concentration limits for drinking water, which the California Environmental Protection Agency (EPA) is now considering (US EPA, 2018).

Environmentally, chromium cannot be biodegraded. Its physical and chemical properties vary in a number of ways when it is exposed to its surroundings. The chemical form of the trace element chromium determines its level of toxicity. Determining the true environmental impact and any toxicity issues is not possible with just total Cr values. This means that in order to ascertain the concentrations of every chromium species in a sample, chromium speciation must be conducted. But determining Cr speciation is a difficult undertaking. Kutsher et al. (2012) found that the stability of certain Cr species can be significantly impacted by the conditions that exist during sample collection and treatment**.** In aqueous

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media, pH and redox conditions influence the ionic state of Cr present in the medium. Under acidic conditions, a high redox potential favour the stabilization of Cr (III), whereas under basic conditions, the redox potential decreases and favours the equilibration of Cr (VI). It has been observed that the soluble Cr (III) depends on pH, where it is insoluble between neutral and alkaline pH. At a pH below 5, Cr (III) predominates, whereas at a higher pH, Cr (VI) is at a higher concentration. Between pH 0 and 4, Cr (III) forms hexacoordinate complexes with several complexing agents, such as organic acids, sulphate, ammonia, and water. At pH 4-6, products of hydrolysis such as Cr $(OH)^{2+}$, Cr $(OH)^{+}_{2}$ and Cr $(OH)_3$ are formed (Unceta et al., 2010). Cr (VI) exists in various oxyanionic forms because it is a strong oxidizing agent. These oxyanionic forms include hydrochromate (HCrO), chromate (VI), and dichromate (VI). The form of Cr (VI) present is dependent on the nature of the environment. For instance, dichromate ($Cr_2O_7^{2-}$) is the prevalent form of Cr (VI) present in acidic conditions, whereas chromate (CrO_4^{2-}) is mostly prevalent in alkaline conditions (Pushkaret al., 2021). The various Cr species present at different pH are presented in Figure 1.1.

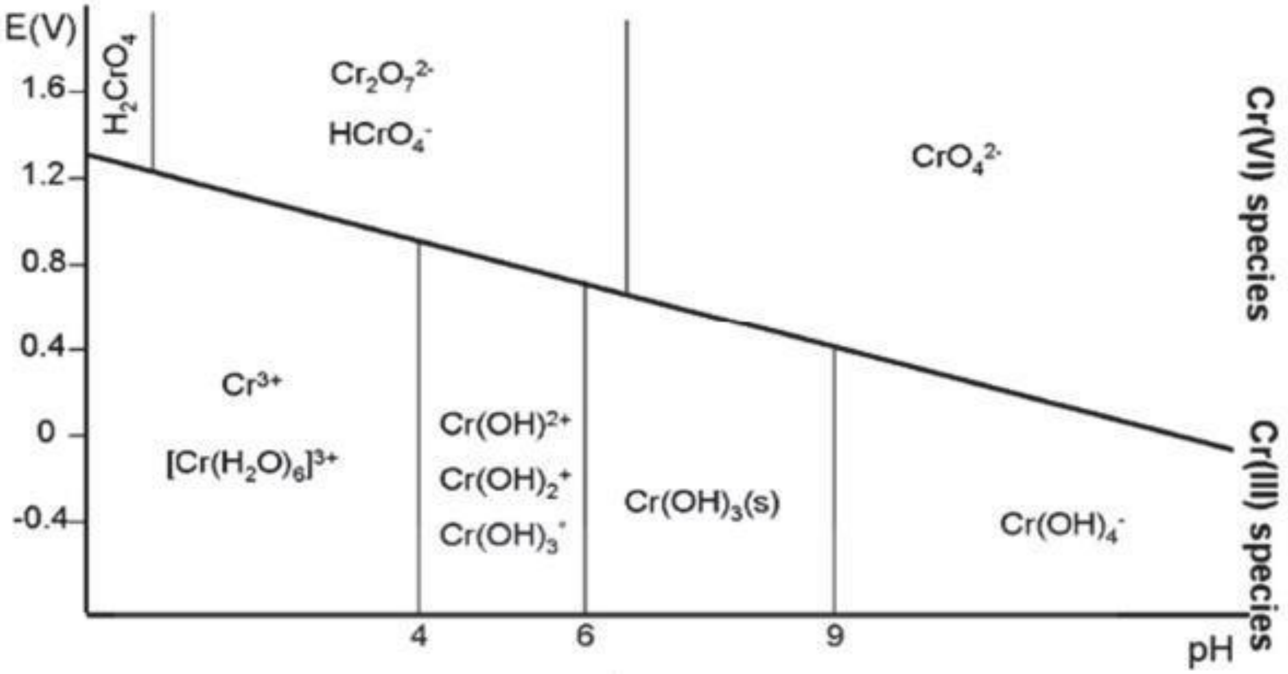

Figure 1.1 Cr (III) and Cr (VI) species as a function of pH and potential (Unceta et al., 2010)

Although measuring total chromium by itself is insufficient to assess the true impact on the environment and associated toxicity hazards. Thus, Cr speciation must be performed in order to ascertain the relative abundances of each chromium species in a sample. However, the investigation of speciation for chromium is a difficult task. The conditions that arise during the collection and processing of samples have the potential to impact the stability of various Cr species (Kutsher et al., 2012). The primary methods of selection that have been identified for the speciation of Cr species are co-precipitation, solvent extraction, solid-phase extraction (SPE), separation via ion exchange, and/or chelating resin. Because of their ease of automation, safety, high enrichment factors, simplicity, and selectivity, solid-phase extraction techniques have been extensively employed (Cimen et al., 2013). In this project, the selective preconcentration of Cr (VI) in water was achieved using chromabond-NH_2 columns. Ambushe et al. (2009) used a chromabondNH_2 column to speciate chromium in milk samples prior to ICP-MS detection. A chromabond-NH_2 column will be used to speciate chromium on three rivers and dam under this project.

1.2 Problem statement

Chromium is naturally occurring element found in different oxidation states, predominantly as trivalent chromium (Cr (III)) and hexavalent chromium (Cr (VI)) in natural water. While Cr (III) is an essential nutrient for humans and is generally non-toxic, Cr (VI) is highly toxic, carcinogenic, and pose significant environmental and health risks. The presence of chromium in natural water source is often attribute to anthropogenic activities such as industrial discharge and improper waste management. Communities around rivers and dams are the ones to suffer from heavy metal exposure, as they mostly depend on water from rivers and dams for survival.

Major challenges lie in differentiating between the different species of chromium in water due to their differing chemical behaviours, toxicities, and environmental impact. Without accurate speciation analysis, the overall chromium concentration in water does not provide adequate information for risk assessment or remediation efforts. This gap creates a critical need for precise analytical techniques to differentiate Cr (III) and Cr (VI) in natural water. This is the first project; no study has been reported on the speciation of chromium species in natural water within Limpopo Province. Therefore, this study focused on Cr speciation from water samples collected from the Mutale river, Luvuvhu river, Dzindi river, and Nandoni dam.

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1.3 Aim and Objectives

1.3.1 Aim:

The main objective of this study is the speciation analysis of chromium in natural water in selected water bodies in Limpopo Province.

Objectives:

1. To determine the physico-chemical composition of the water in selected bodies
2. To determine the total concentration of Cr in water samples using ICP-OES
3. To speciate Cr (III) and Cr (VI) in water samples using FAAS
4. To compare different concentrations of Cr obtained with the ones from WHO and SABS

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1.4 Motivation of the study

Water is essential to sustaining life. Providing safe and high-quality water and its convenient availability is an essential entitlement for every individual. Approximately 15% of the global population resides in regions experiencing water stress, as reported by Schwarzenbach et al. (2006). Most rural communities in developing nations rely on water from rivers, dams, and agricultural needs, which are not treated. Because Cr (VI) is poisonous, it is very important to determine its species selectively. Therefore, it is necessary to determine the speciation of chromium in water so that the communication and local municipalities can be altered if the water that they are using is clean or not. Chromium speciation is very important as it reveals which chromium species is more or less in water.

Mohsin et al. (2013) found that the amount of water in emerging African countries is declining significantly, while the quality of water is deteriorating rapidly as a result of growing urbanization, deforestation, and land degradation. Water quality for drinking is continuously being affected. Heavy metal exposure commonly arises from the consumption of contaminated drinking water. Water may contain excessive levels of heavy metals that exceed the permissible limit for drinking water, posing risks to human health, plants, animals, and the environment.

Determining water composition is very important, as it also helps us as human beings determine what type of water we are using, which elements are present, and whether it is good for us or not. This project contributes to the Sustainable Development Goals (SDGs) and National Development Plan (NDP), and it will help us to understand more about the speciation of chromium and identify the species that is toxic to human health.

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CHAPTER 2: LITERATURE REVIEW

Introduction

This chapter provides an overview of the theory and research on speciation of chromium in water. Moreover, it provides an overview of the IC, ICP-OES, AAS, and XRF are given, along with their principles.

2.1. Theory

Speciation analysis is the process of finding or quantifying the concentrations of specific chemical species in a given sample. As defined by Gonzalvez et al. (2010), speciation of analytically identifying and quantitatively measuring the different chemical forms of elements in a given sample. The study of speciation has gained significant attention in recent years, primarily because of the distinct behavioural variations exhibited by different chemical species of a specific element. Speciation analysis is a crucial chemical technique employed in analytical laboratories across various disciplines such as environmental science, food science, geology, pharmacy, and medicine.

The ideal procedure for speciation would deliver the required species information while maintaining the original sample's identity. In the absence of such a method, speciation has been accomplished by the application of a combination of analytical and methodological approaches, such as chromatographic separation, spectroscopy, and fundamental chemical operations. These methods are well-established and involve both non-chromatographic and chromatographic approaches. Without speciation knowledge, no meaningful interpretation of biological or geochemical processes can be established (Sica et al., 2019).

Chemical speciation is a critical area of study in environmental protection (Jabłońska-Czapla et al., 2014). Toxicological and analytical research is necessary because the chemical forms in which trace elements are found, affect their toxicity, availability, and reactivity. The speciation analysis is discernible and can educate individuals about the consequences of the chemicals they use on the environment and how those consequences will affect their own health.

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2.2. Chromium

Understanding the fate and exposure of chromium in polluted ecosystems becomes crucial. The predominant oxidation states of chromium found in environmental matrices are hexavalent Cr (VI) and trivalent Cr (III). Even in small concentrations, Cr (VI) is dangerous to humans as it travels from the soil to water and finally to humans. The trivalent Cr (III) and hexavalent Cr (VI) species are the most stable forms of chromium. Chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) oxyanions are the most poisonous forms of Cr (Mathur et al., 2016). Chromium (III) exhibits lower mobility and has a reduced hazard level. It is predominantly in soil and water, typically bound to organic substances.

Chromium speciation is crucial for ensuring the safety of human food and water supplies. Chromium (VI) is genotoxic and mutagenic to biological systems, but Cr (III) plays a crucial function; glucidic metabolism in humans and is far less toxic (Yang et al., 2013). Chromium (III) is important in lipid, protein, and carbohydrate metabolism (Mahmoud et al., 2008). In terms of acute and chronic oral toxicity, skin irritancy and allergy, systemic effects, cytotoxicity, genotoxicity, and carcinogenicity, chromium (VI) compounds are more harmful than chromium (III) compounds (Costa and Klein, 2006).

2.2.1 Major uses

Chromium is widely used in the metals, chemicals, and refractory sectors. Numerous environmental systems contain chromium as a pollutant due to its extensive use in numerous industrial processes (Sonone et al., 2020). Chromium compounds are utilized in leather tanning, wood preservation, dyes and pigments, and chromium plating, among other applications. For the preservation of wood, chromium (VI) salts are utilized despite their toxicity. An instance of the application of chromated copper arsenate (CCA) in timber treatment is to safeguard timber against decomposition fungi, termites, and marine borers (Hingston et al., 2001). Leather tanning requires chromium (III), chrome aluminium and chromium (III) sulphate. Chromium (III) serves to stabilize the leather through the process of cross-linking the collagen fibers (Liang et al., 2014). Trivalent chromium (Cr (III))-based dietary supplements are widely utilized as mineral supplements for humans, especially for weight loss and performance enhancement. Standard audio cassettes and high-performance audio tape both use magnetic tape based on chromium (IV) oxide.

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2.2.2 Toxicity

Exposure to chromium can occur by inhalation of chromium-containing air or through skin contact with chromium compounds. Symptoms of high chromium levels in the body include liver problems, thrombocytopenia, renal failure, rhabdomyolysis, haemolysis, changes in thought processes, chest pain, gastrointestinal disorders, erythema/flushing/rash, headache, dizziness, and agitation (Megharaj et al., 2003; ATSDR, 2000). Bigorgne et al. (2010) showed that trivalent chromium exhibited genotoxic effects on Eisenia fetida earthworms when exposed to natural soils for four days. Excessive ingestion of Cr (III) can cause considerable genotoxic danger in both animals and humans (Eastmond et al., 2008).

Hexavalent chromium, on the other hand, is exceedingly hazardous to both humans, plants, and animals. Chromium (VI) is widely regarded as the most poisonous form of chromium, typically found in combination with oxygen as chromate. Exposure to organic contaminants causes the conversion of chromium (VI) to Cr (III). Chromium (VI) diffuses across the cell membrane, acts as an oxidizing agent, and binds to other biological molecules in the body, resulting in carcinogenic and mutagenic consequences. Hexavalent chromium enters the body via a sulphate anion carrier system and is quickly taken up by cells due to its high solubility (Leese, 2018). According to Casadevall et al. (2002), the creation of hydrogen peroxide during the reduction of chromium species in cells may result in the generation of reactive species with DNA-damaging potential. Breathing excessive quantities of chromium (VI) can induce nasal lining irritation and ulceration. Drinking water contaminated with chromium (VI) causes a high risk of stomach cancer in humans and animals.

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2.3. Relevant studies

Bertoia (2003) investigated the identification of inorganic arsenic and chromium species in US groundwater using ion chromatography-inductively coupled plasma mass spectrometry (IC - ICPMS). The groundwater samples exhibited an overall chromium concentration ranging from 0.25 mg/L to 4 mg/L, with most of the samples possessing more elevated levels of hexavalent chromium than trivalent chromium.

Ying and Xiashi (2011) conducted a study on the speciation of Cr (III) and Cr (VI) ions. They utilized βcyclodextrin-crosslinked polymer micro-column and graphite furnace atomic absorption spectrometry in China. The concentration of Cr (VI) was determined by subtracting the Cr (III) concentrations from the total chromium concentrations. Analysis revealed that chromium content in tap water was measured at 0.56 μgL^{-1} for Cr (III), whereas no traces of Cr (VI) were found.

Sea et al. (2019) used ion chromatography-inductively coupled plasma mass spectrometry to detect chromium species in water and plant samples at low concentrations in Turkey. The study revealed varying chromium concentrations in different sources, such as springs, tap water, and plants. Separation was achieved using an anion exchange column with a mobile phase of 0.55 M HNO_3^-. The results demonstrated chromium concentration in spring, tap, and plants. In water, the concentration ranged from 99.3 ± 4.6 for Cr, and in simulated gastric fluid, the concentration of chromium released from plants was 12.74 ± 0.59 for Cr (III) and 17.49 ± 0.45 for Cr (VI).

Mokgohloa (2019) examined chromium speciation in water and sediments from the Mokolo and Blood rivers in Limpopo Province, South Africa. Samples were analysed using flame atomic absorption spectroscopy (FAAS) and graphite-furnace atomic absorption spectroscopy (GFAAS). The amounts of Cr in water and sediment samples obtained from Blood River ranged from 1.56 to 6.11 µg/L and 129.2 to 252.9 µg/L, respectively. The chromium values in water and sediment samples collected from the Mokolo river varied between 1.34 and 3.53 µg/L and 25.7 and 156.4 µg/L, respectively.

Mandina and Mugadza (2013) investigated the process of speciation of chromium in soils, plants, and wastewater at a ferrochrome slag dump in Gweru. Determining the different forms of chromium in plant leaves, soil, and slag samples involved extracting Cr (VI) selectively by employing a sodium carbonate leaching method. This was done before measuring the concentration of Cr (VI) using spectrophotometry.

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The samples were tested for total chromium and chromium (III) levels using flame atomic absorption spectroscopy. The mean content of Cr (VI) in soil samples is 1.0301 ± 0.0854 µg/L, while in plant samples it is 0.3372 ± 0.0168 µg/L.

2.4. Instrumentation for analysis of Cr

2.4.1. Inductively coupled plasma optical emission spectrometry (ICP-OES)

The ICP-OES has been extensively used to analyse Cr in various environmental samples. This method provides precise and reliable measurements of chromium concentrations, which is crucial for assessing its potential hazards in water from rivers and dams. The method involves the excitation of chromium atoms in a high-temperature plasma, where they emit characteristic wavelengths of lights that can be measured to determine concentration. ICP -OES has been particularly effective in the analysis of chromium contamination in water bodies, analysing industrials effluents, and studying the bioavailability of chromium in food production. ICP – OES analysis the distribution of chromium species in wastewater treatment plant, revealing critical insights into the reduction of toxic Cr (VI) to the less harmful Cr (III) during the treatment processes (Clark and Lee, 200).

The principle of operation includes sample introduction; the sample, typically in liquid form, is introduced into the ICP-OES system using a nebulizer, which converts the liquid sample into a fine aerosol, Plasma Generation; The aerosol is carried by an argon gas stream into the inductively coupled plasma (ICP). The plasma is generated by a radiofrequency (RF) coil that ionizes the argon gas, creating a high-temperature environment (approximately 10,000 K). Atomization and Excitation: in the plasma, the sample aerosol undergoes desolvation, vaporization, atomization, and excitation. The high energy of the plasma breaks down the sample into its constituent atoms and ions, which are then excited to higher energy levels.

Emission of Light: As the excited atoms and ions return to their ground state, they emit light at characteristic wavelengths. Each element emits light at specific wavelengths, allowing for their identification and quantification, Detection and Analysis: The emitted light is collected and directed through a spectrometer, which separates the light into its component wavelengths. A detector measures the intensity of the emitted light at these wavelengths. The intensity of the light is proportional to the concentration of the element in the sample and lastly, Data Processing; The detected signals are processed by a computer, which compares

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them to calibration standards to determine the concentration of chromium and other elements in the sample. Figure 2.1 provides an overview of the various components.

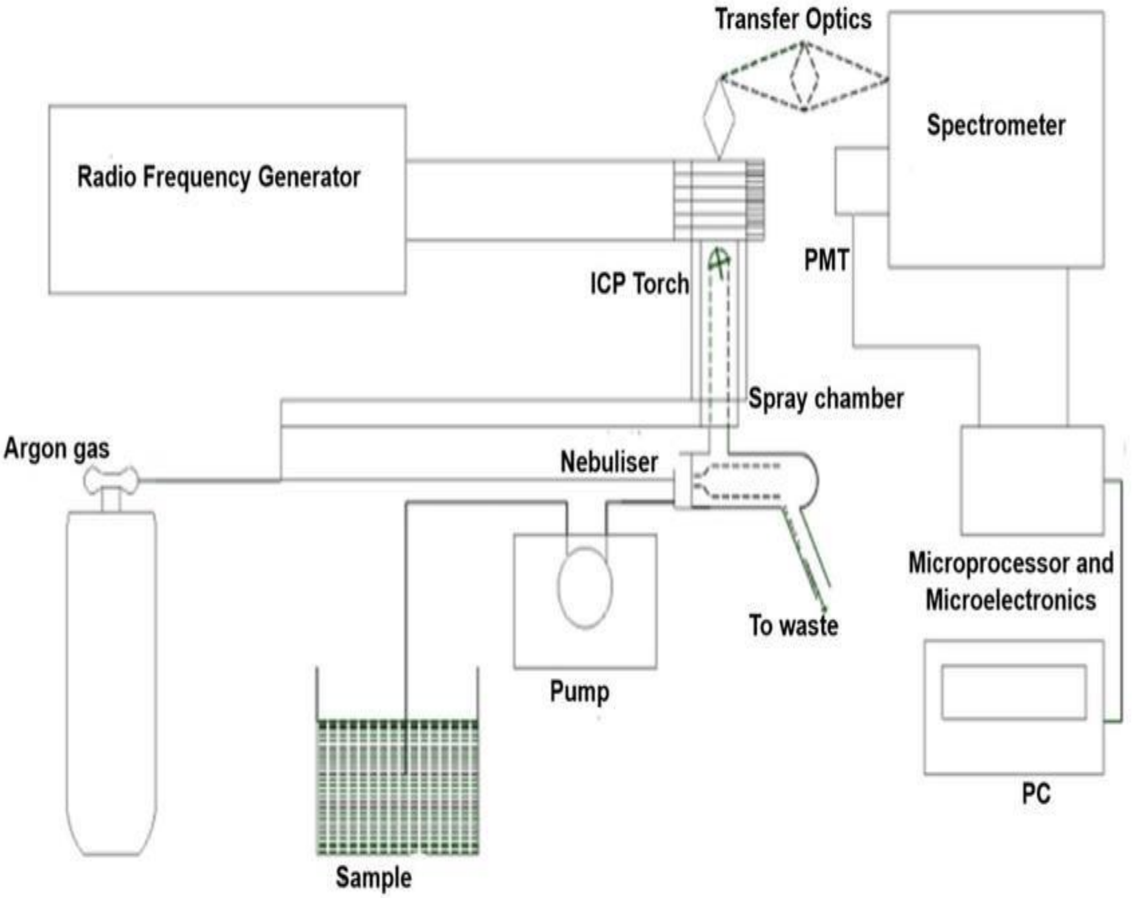

Figure 2.1. The components of Inductively coupled plasma - optical emission spectroscopy (ICP-OES). (Nyika et al., 2019)

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2.4.2. Flame atomic absorption spectrometry (FAAS)

Flame atomic absorption spectrometry (FAAS) is an analytical technique that examines the absorption of radiation (light) by atoms in a gaseous state in order to detect chemical components present. In this case, the method is utilized to determine the amount of chromium in water samples. Flame atomic absorption spectrometry is frequently used to identify trace elements since it is simple to automate, affordable, has a low detection limit, and can quickly resolve minor interferences (Garcia and Baez, 2012). One disadvantage of adopting FAAS is that it takes a long time to investigate each component.

FAAS uses a light beam emitted by the source that must have the correct wavelength for measurement as it passes through the flame containing the element in its atomic form. The beam is then focused at the monochromator's entrance aperture. A monochromator selectively isolates the exact wavelength of light absorbed by the sample by filtering out all other wavelengths. Selecting a certain wavelength of light allows you to correctly identify the exact element of interest even in the presence of other constituents. The monochromator directs light to a detector. Photomultiplier tubes are widely used as detectors to convert light signals into electrical signals that are proportional to the intensity of light (Martinenghi et al., 2016; Garcia and Baez, 2012).

Particularly during pre-concentration procedures, Cr species concentrations that are comparatively low may undergo modification during sample handling and analysis. For preconcentrating and separating two main chromium species, total chromium and chromium (VI), atomic spectrometric detection is the most frequently referenced technology in the scientific literature, either by itself or in conjunction with other methods. Figure 2.3 shows the fundamental components of FAAS.

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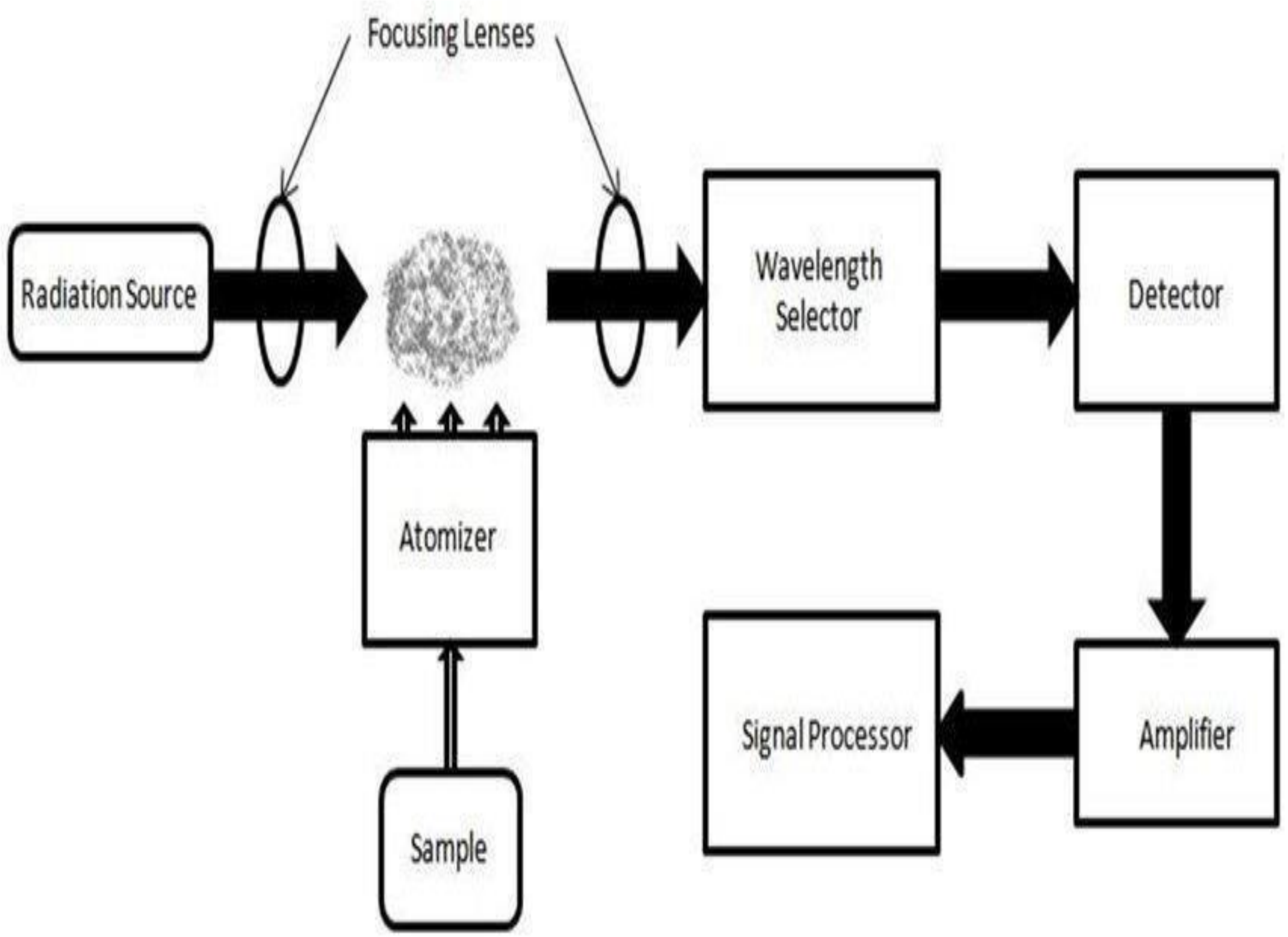

Figure 2.2: Schematic diagram of flame – atomic absorption spectrometry (FAAS) (Walker et al., 2016).

2.5. Water sampling methods

Traditional method:

Traditional methodology was and continues to be extensively employed by researchers at present. Conventional methodologies, including the capture technique, require substantial volumes of water to be transported from sampling locations to laboratories, where they are extracted and analysed using instruments (Vrana et al., 2005). Typically, samples are acquired through the immediate refilling of the sample container. Conversely, pumps (peristaltic pumps capable of gathering greater volumes of water) could be employed in lieu of this technique due to its unsuitability for deep water conditions.

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Passive-sampler Method:

Passive sampler is a device designed to collect and measure contaminants like chromium and other metals in various environmental media (e.g., water, air, and soil) without the need for active sampling or pumping. They are particularly useful for monitoring trace metals concentrations over time, providing a cost effective and efficient approach for long – term environmental monitoring. Polymeric ion-exchange membrane (PIMs), diffusion-gradient in thin films (DGTs), and semi-permeable membrane devices (SPMDs) are all types of passive sampling methods. The DGT use semi-permeable membranes that allow metals to pass through and be captured by an absorbent or reactive layer inside the sampler, as it is designed to monitor metals like chromium, lead, cadmium, and copper. PIMs consist of a polymer matrix embedded with ion-exchange ligands. These ligands selectively bind the metal ions from the surrounding environment during the exposure. The selective uptake depends on the chemical properties of the membrane and target metals, and it is used in metals like Cr, Ni and Cu in water system

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CHAPTER 3: Methodology

Introduction

This chapter focuses on the experimental procedure. This chapter provides a comprehensive overview of the sampling areas, including detailed information on samples collections, preparations and analytical procedure.

3.1. Sampling area description

The Dzindi, Mutale, and Luvuvhu rivers, along with the Nandoni dam, form an important hydrological network in the Limpopo Province of South Africa. Dzindi and Mutale rivers; these rivers do not directly flow into the Nandoni dam. However, they contribute to the broader hydrological system that ultimately influences the water quality and volume in the region. The Luvuvhu river directly feeds into the Nandoni dam, making it a critical source for the reservoir. Here is a detailed discussion of each of these sampling points, including their characteristics, significance, and sampling locations.

Dzindi river:

The Dzindi river is a smaller river in Limpopo Province. It plays a crucial role in local agriculture and sustains various ecosystems along its course. The river is subject to seasonal fluctuations and is extensively used for irrigation by the local communities. Sampling Coordinates: S23° 02.15', E30° 32.56': Midstream, this site captures the impact of agricultural runoff and community usage.

Mutale river:

The Mutale river is known for its clear waters and diverse aquatic life. It flows through rural areas, supporting both agriculture and wildlife. It is vital for the local biodiversity and serves as a water source for nearby communities. Sampling Coordinates: S22° 52.76', E30° 28.49': Midway, where agricultural influence is moderate.

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Luvuvhu river:

The Luvuvhu river is a significant river in the region, known for its length and the variety of ecosystems it supports. It traverses through diverse landscapes, including urban areas, farms, and wildlife reserves. Sampling Coordinates: S23° 05.89', E30° 19.54': Midstream, influenced by urban and agricultural activities.

Nandoni dam:

Nandoni dam, also known as the Vondo dam, is a large dam on the Luvuvhu river in Limpopo Province. It is crucial for water supply, irrigation, and flood control in the region. The dam creates a significant reservoir that supports various water needs, including domestic, agricultural, and industrial uses. Sampling Coordinates at the Dam: S23° 15.67', E30° 30.89': Mid-reservoir, for overall water quality assessment.

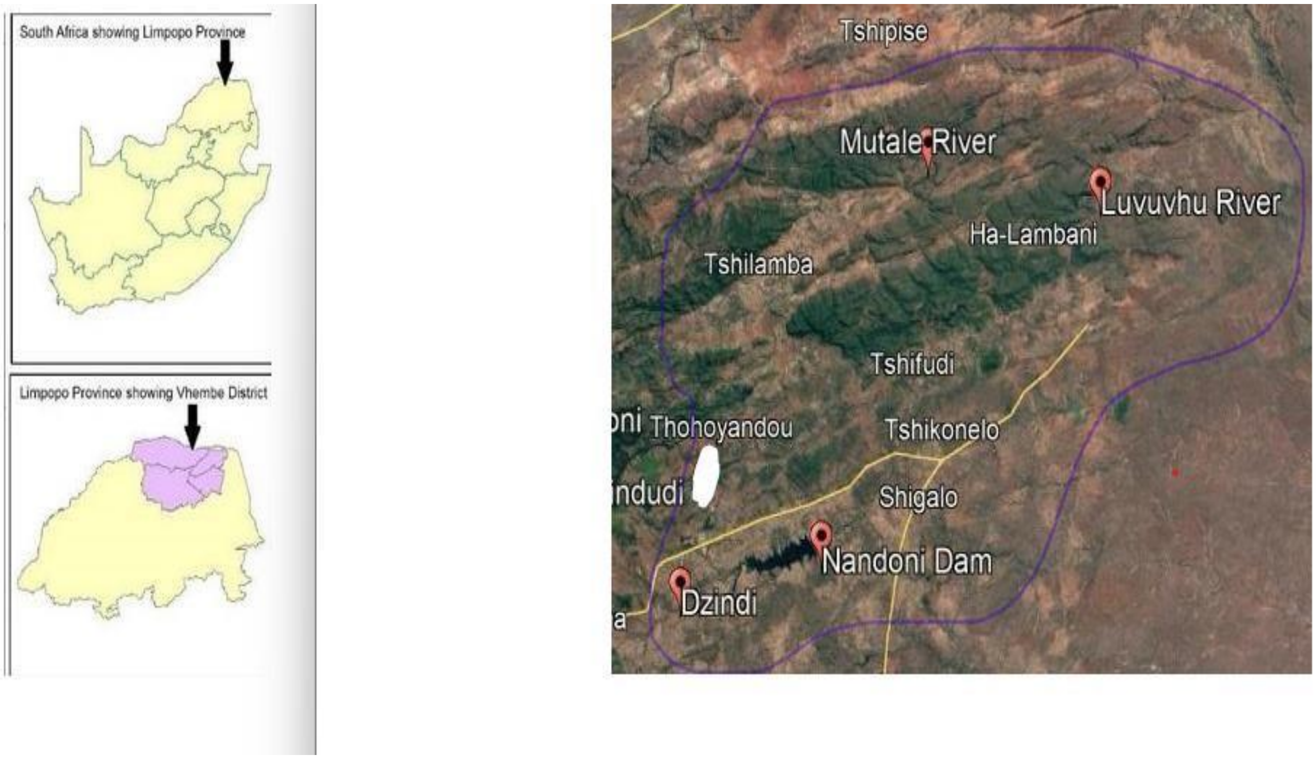

Figure 3.1: Sampling points around the Vhembe district, Limpopo province, South Africa.

3.2. Sample collection and sample preparation.

The samples were collected during the dry and rainy seasons. Water samples were collected using 500 mL plastic bottles that were sensed thoroughly using deionized water and dilute HNO_3^-, Grab method was adopted for sampling. Thermometers were only used to measure the temperature. The pH, TDS, EC, and dissolved oxygen were measured using the multiparameter photometer and pH meter in the laboratory, and samples were preserved using HNO_3^- for anions and cations, respectively. The samples were stored in a cooler box, during transportation, and in the laboratory, they were stored in the fridge.

3.3. Laboratory analysis

3.3.1. Inductively coupled plasma optical emission spectrometry analysis

The concentrations of metal cations were determined using a Spectro ARCOS ICP-OES (Cleve, Germany) with a radial plasma view. The radio frequency generator power (1400 W), pump speed (30 rpm), plasma gas flow rate (13 L min^{-1}), auxiliary flow rate (2 L min^{-1}) and nebulizer flow rate (0.95 L min^{-1}) were the best operating parameters for the ICP-OES analysis. For a 12 second integration period, the solution absorption rate was 2.0 mL min $^{-1}$. Table 3.1 shows the operation conditions used for the analysis of ICPOES.

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Table 3.1 Essential operating condition of the ICP-OES.

Parameters	Setting
Power (W)	1450 W
Nebulizer flow (Ar)	0.71 L min^{-1}
Nebulizer	Modifed Lichte
Spryay Chamber	Double pass cyclonic
Torch injector diameter	1.8 mm
Sample uptake rate	2.0 mL min^{-1}

3.3.2. Flame atomic absorption (FAAS) analysis.

FAAS was used to determine chromium concentrations in water samples according to the parameters indicated in Table 3.2. The amounts of chromium (Cr) in all samples were measured using an external calibration curve. The blank, standards, and all sample solutions were aerosolized and then washed with deionized water for at least 1 minute. This was done to sanitize the sample device and avoid contamination of future solutions. Each sample's concentrations were determined by measuring three replicates and then calculating the average value. Blanks were likewise examined, and the intensity of each analyte in the blank sample was subtracted from that of the sample.

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Table 3.2: Instrumental operating conditions for FAAS.

Parameters	Setting
Flame type	Air-C_2H_2
Wavelength (nm)	357.90
Slit width (nm)	0.70
Lamp current (Ma)	20
Mode	Peak height
Air flow rate (mL/min)	6.0
Acetylene flow rate (L/min)	2.0

3.4. Speciation of Cr (VI) and Cr (III) and quantitation using FAAS

Cr (VI) separation in water was performed using the solid-phase extraction (SPE) technique with a chromabond-NH_2 column. A mixture of Cr (III) and Cr (VI) standards, each at a concentration of 0.5 µg/L in 100 mL of de-ionized water, was combined with 5 mL of a 0.001% solution of alizarin sulphonic acid. The pH of the sample solution was modified to 5.5 by utilizing an acetic acid and sodium acetate buffer. The column was conditioned by passing two times the volume of the column with a 1 M solution of nitric acid, followed by two times the volume of de-ionized water. The column could quantitatively retain Cr (VI) by running the sample through it at a flow rate of 3 mL/min. Following the adsorption of the sample, the contents of the column were subjected to vacuum drying. The hexavalent chromium (Cr (VI)) was separated by passing two times the volume of the column with a solution of 2 M nitric acid (HNO_3). A 100 mL water sample was combined with a 5 mL solution containing 0.001% alizarin sulphonic acid. pH was adjusted to 5.5 using an acetic acid and sodium acetate buffer.

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CHAPTER 4: RESULTS

Introduction

This chapter discusses the physio-chemical, soil sample results, ICP-OES, and FAAS results. The first part (4.1) explains the physicochemical properties of water, whereas the second part (4.2) describe the results of Cr analysed by IPC-OES and third part (4.3) describe the results of Cr analysed by FAAS.

4.1 Physicochemical properties of waters

The fundamental physical and chemical properties of water are referred to as its physiochemical properties, which include pH, temperature, total dissolved soil, and electrical conductivity. Several of these physiochemical features are readily available in the literature and are mostly attributable to the intermolecular hydrogen bonding that exists between water molecules. However, some of these "physicochemical properties" change depending on the water source. Four physiochemical properties were examined in samples from the Dzindi, Luvuvhu, Mutale, and Nandoni dams: pH, temperature, total dissolved solids (TDS), and electrical conductivity (EC). Tables 4.1 and 4.2 show the results obtained during the dry and rainy seasons for temperature, pH, TDS, and EC.

Table 4.1: Results for physicochemical parameters (Temperature, pH, total dissolved soil and conductivity) dry season.

Samples site	pH	Temperature (°c)	TDS (mg/L)	EC (µs/cm)
Dzindi River	7.54	23	74.6	123.2
Luvuvhu River	7.78	24.3	109.0	153.3
Mutale River	7.45	23.6	71.3	89.5
Nandoni Dam	8.25	24	102.0	147.6

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Table 4.2: Results for physicochemical parameters (Temperature, pH, total dissolved soil and conductivity) rainy season.

Samples site	pH	Temperature (°c)	TDS (mg/L)	EC (µs/cm)
Dzindi River	7.72	20	85.1	171.2
Luvuvhu River	8.30	24.3	123	175.1
Mutale River	7.61	23	56.7	85.5
Nandoni Dam	7.94	22	129	182.5

The temperature is a measure of the heat content of the water. It is important as it affects the physical and chemical properties of water, including the solubility of gases (e.g., oxygen), chemical reaction rates, and the metabolic rates of aquatic organisms. Temperature also influences the stratification and mixing patterns in water bodies. Natural water bodies exhibit seasonal and diurnal variations in temperature; therefore, in this study, the temperature is exhibiting seasonal variations. During both the dry and rainy seasons, the temperature for all samples varied from 20 ºC to 24 ºC (Tables 4.1 to 4.2). There was no significant difference between the dry and rainy seasons.

pH is a measure of the hydrogen ion concentration in water. It indicates the acidity or alkalinity of water on a scale from 0 to 14, with 7 being neutral. Values below 7 indicate acidic conditions, while values above 7 indicate alkaline conditions. It is important as it affects the solubility and biological availability of chemical constituents such as nutrients and heavy metals. It also influences the effectiveness of water treatment processes and the health of aquatic ecosystems. The pH of natural waters usually ranges from 6.5 to 8.5, but a deviation from this range can indicate pollution or environmental issues. Therefore, in this study, the pH of the rivers (Dzindi, Luvuvhu, and Mutale) was virtually neutral, while the pH of Nandoni dam was alkaline during the dry season and virtually neutral during the rainy season. During both dry and rainy seasons, pH for all water samples (Tables 4.1 and 4.2) was within WHO (2008), SANS 241 (2006), and Canadian drinking water quality guidelines. During both the dry and rainy seasons.

Total Dissolved Solids (TDS) represent the combined content of all inorganic and organic substances contained in a liquid, including minerals, salts, and organic matter. It is important as it is an indicator of water quality, affecting the taste, hardness, and corrosiveness of water. High TDS can affect the health of aquatic life and the suitability of water for drinking, irrigation, and industrial uses. TDS levels in natural

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waters can vary widely from less than 1000 mg/L, with values above this indicating potential pollution or high mineral content. In this study, the results of the TDS level were within WHO water guidelines during the rainy season.

Electrical conductivity (EC) measures the ability of water to conduct electricity, which is directly related to the concentration of dissolved ions in the water. It is important as it is a quick and reliable indicator of the total ion concentration (i.e., TDS) in water. It helps in assessing the purity of water and identifying pollution sources. In general, EC values reflect the presence of dissolved ions in water, which can impact water flavour and contribute to water hardness. Water with high EC levels should not be used in households. EC values vary depending on the ionic composition and concentration in the water. Natural water has very low conductivity, while seawater, with its high salt content, has high conductivity. The natural waters generally show EC values ranging from 50 to 1500 µS/cm, depending on geological and environmental conditions. In this study, the results of EC for both the dry and rainy seasons ranged from
50 to 1500 µS/cm. Although the results in the rainy season were higher than those in the dry season, all were within the estimated range according to WHO guidelines.

The TDS and EC have a positive correlation. TDS in samples increases with increasing EC. TDS levels contribute to aquatic system pollution. Conductivity is important for estimating TDS because of the current conduction in an electrolyte solution (Hayashi, 2004). The values of TDS in Dzindi river samples and Mutale river samples fell within WHO standard guidelines and were 74.6 mg/L and 71.3 mg/L (for dry season) and 85.1 mg/L and 56.7 mg/L (for rainy season). The samples from the Nandoni dam and the Luvuvhu river were found to have greater levels of electrical conductivity and total dissolved solids. The EC and TDS values from Luvuvhu river in Tables 4.1 and 4.2 were 153.3–175.1 µs/cm and 109–123 mg/L, as for Nandoni dam, 147.6–182.5 µs/cm and 102–129 mg/L for both seasons, respectively. The EC and TDS levels in all samples were below the WHO, SANS, and Canadian drinking water quality guidelines.

Monyai et al. (2016) investigated the water quality of the Luvuvhu river and its tributaries within the Thulamela Local Municipality. pH values recoded for Dzindi and Luvuvhu rivers were 7.36 and 7.32, and TDS were 85.80 mg/L and 105.20 mg/L. The pH values for Dzindi and Luvuvhu rivers are not significantly different from those presented in Tables 4.1 and 4.2, indicating that the sample water from Dzindi and

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Luvuvhu rivers has experienced deterioration. The TDS values for Dzindi and Luvuvhu rivers are also not too different from the ones shown in Table 4.1 above.

Gumbo et al. (2016) studied physico-chemical properties from the Dzindi river and Luvuvhu river. pH, TDS, and EC, which are 7.60 and 7.40, 33.3 and 26.2 µs/cm, and 4.9 and 4.2 mg/L were recorded. The temperature ranged from 23 ºC to 24 ºC. The area has not experienced climate change and has maintained its temperature for the past 10 years. That is why the temperature in this study also ranged from 18 ºC to 24 ºC. The pH results that were found in the Dzindi river were similar to the results obtained in the Luvuvhu river (table 4.1) in the sense that both pH's indicate the sample water from Dzindi and Luvuvhu rivers is mildly alkaline. As for TDS and EC values, which are much lower than in this study (Table 4.1), they are mighty due to high rainfall.

4.2. Inductivity coupled plasma - optical emission spectrometry (ICP - OES)

4.2.1. Calibration of ICP-OES standards solution

The instrument was calibrated using the following standard solutions: 0, 2, 4, 6, 8, and 10 mg/L. Table 4.3 shows calibration data for selected elements. The linearity technique was established by employing seven calibration standards and the resulting linear coefficients of determination (R^2). All chosen cation standards had R^2 values around 0.964 up to 0.999, suggesting that the technique was acceptable for cation determination.

Table 4.3: Calibration of selected metals wavelength line (nm) from the ICP-OES analysis

Analytes	Wavelength (nm)	Correlation coefficient
Arsenic	189.042	0.988
Chromium	206.149	0.999
Uranium	385.9570	0.987
Iron	259.940	0.993
Aluminium	396.152	0.964

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4.2.2 Determination of selected metals in river samples by using ICP – OES

Table 4.4: Concentration of selected metals in water samples (dry season)

Sampling site	Chromium (mg/L) ± SD	Uranium (mg/L) ± SD	Arsenic (mg/L) ± SD	Iron (mg/L) ± SD	Aluminium (mg/L) ± SD
Dzindi River	2.607 ± 0. 134	4.726 ± 0.172	0.914 ± 0.034	3.246 ± 0.153	4.103 ± 0.227
Mutale River	3.441 ± 0.173	4.280 ± 0.253	3.492 ± 0.210	4.941 ± 0.268	3.548 ± 0.174
Luvuvhu River	2.564 ± 0.183	3.434 ± 0.216	4.869 ± 0.264	3.151 ± 0.190	1.557 ± 0.073
Nandoni Dam	4.613 ± 0.236	5.251 ± 0.324	-1.314 ± 0.024	4.324 ± 0.258	6.228 ± 0.423
WHO guideline	0.05	0.03	0.01	0.3	0.2

Table 4.5: Concentration of selected metals in water samples (rainy season)

Sampling site	Chromium (mg/L) ± SD	Uranium (mg/L) ± SD	Arsenic (mg/L) ± SD	Iron (mg/L) ± SD	Aluminium (mg/L) ± SD
Dzindi River	3.687 ± 0.174	6.862 ± 0.479	8.170 ± 0.514	5.173 ± 0.314	6.857 ± 0.423
Mutale River	5.667 ± 0.324	3.324 ± 0.213	7.334 ± 0.493	5.891 ± 0.340	7.647 ± 0.482
Luvuvhu River	5.44 0± 0.291	6.103 ± 3.914	10.493 ± 0.712	4.244 ± 0.210	3.383 ± 0.191
Nandoni Dam	6.803 ± 0.462	6.579 ± 0.410	0.631 ± 0.091	4.280 ± 0.235	2.231 ± 0.113
WHO guideline	0.05	0.03	0.01	0.3	0.2

Major element concentrations such as Cr, As, Fe, U, Al, were determined by ICP-OES analysis of samples, that affect the speciation of chromium. Using competitive sorption or complexation reactions, these elements can change the oxidation state of chromium, form complexes with it, and affect its speciation. Knowing these components is essential for risk assessments related to the environment and human health because the toxicity and bioavailability of various species varies. The comprehensive understanding of the

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chemistry and behaviour of the system that results from combining various element analysis aids in the prediction and management of the effects on the environment and human health. Chromium often coexists with other metals in industrial effluents, mining activities, and natural deposits. Analysing these elements together helps in understanding the overall contamination levels and the potential for complex formation or competitive adsorption on soil and sediment particles (Sun et al., 2019). Analysing metals like arsenic (a known toxin) alongside Cr offers a more comprehensive understanding of potential risk. Table 4.4 shows the data achieved during the dry season, whereas Table 4.5 shows the results obtained during the rainy season.

4.2.2.1. Mutale river

The selected heavy metals (Cr, As, Fe, U, and Al) average concentrations in Mutale river samples were 3.441 ± 0.173, 3.492 ± 0.210, 4.941 ± 0.267, 4.280 ± 0.253, and 3.548 ± 0.174 mg/L, as shown in Table 4.4, in the dry season. During the rainy season, concentrations of selected metals (Cr, As, Fe, U, and Al) were 5.667 ± 0.324, 7.334 ± 0.493, 5.891 ± 0.340, 3.324 ± 0.213, and 7.647 ± 0.482 mg/L, respectively (Table 4.5). The concentrations of selected metals (Cr, As, Fe, U, and Al) during the rainy season (Table 4.5) in the Mutale river were higher; therefore, those sources containing these metals were washed and dissolved into the river due to rain.

In addition, Cr concentrations were all above the water standard guideline. As a result of the Cr result, health implications for the general population are expected**.** It was observed that during the rainy season, there was an increase in Cr concentration. High concentrations of chromium may be due to exposure to industrial wastes or agricultural operations that employ chromium-containing substances such as fertilizers and chromium containing insecticides. Given the presence of agricultural operations and urban wastes along the Mutale river, it is reasonable to presume that arsenic from these sources contributed to the present levels of arsenic. The ascending order of abundance in the Mutale river is U < Cr < Fe < As < Al.

4.2.2.2. Dzindi river

The concentrations of selected heavy metals (Cr, As, Fe, U, and Al) in the Dzindi river were 2.607 ± 0134, 0.914 ± 0.034, 3.246 ± 0.153, 4.726 ± 0.172 and 4.103 ± 0.227 mg/L, respectively, in the dry season (Table 4.4). whereas in the rainy season, concentrations were 3.687 ± 0.174, 8.170 ± 0.514, 5.173 ± 0.314, 6.862

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± 0.479, and 6.857 ± 0.423 mg/L, respectively. During the rainy season, all concentrations were higher compared with the dry season. The rainy season could have led to an elevation of all selected metal concentrations. Chromium (Cr) concentrations for all the seasons were above the drinking water guideline. The increase in chromium content might be attributable to the fact that chromium has several industrial applications, including steel alloys, stainless steel, corrosion-resistant plating, pigments, and dyes. As a result of this extensive use, polluted industrial waste effluent can contribute to excessive chromium levels in surface waterways and drinking water. According to Edokpayi et al. (2016), the Cr concentration in the Dzindi river varied from 0.03-0.10 mg/L, which was well below the drinking water limit.

4.2.2.3. Luvuvhu river

Additionally, the concentrations of selected heavy metals (Cr, As, Fe, U, and Al) in Luvuvhu river samples during the dry season were 2.564 ± 0.183, 4.869 ± 0.264, 3.151 ± 0.190, 3.434 ± 0.216, 1.557 ± 0.073 mg/L. Throughout the rainy season, the concentrations were 5.440 ± 0.291, 10.493 ± 0.712, 4.244 ± 0.210, 6.103 ± 3.914, and 3.383 ± 0.191 mg/L, respectively. The Cr contents in the water exceeded water standard limits. Table 4.5 above shows higher concentrations than the dry season due to rain fall, which causes the wash off of various substances that pollute the environment and end up in rivers and dams, resulting in high metal concentrations. Research carried out in African rivers has revealed elevated levels of Cr, which have been linked to human activity (Greenfield et al., 2012; Kekana, 2013; Shanbehzadeh et al., 2014; Mekonnen et al., 2015).

4.2.2.4. Nandoni dam

During the dry season, the concentrations of selected elements (Cr, As, Fe, U, and Al) in Nandoni dam were 4.613 ± 0.23, -1,314 ± 0.024, 4.324 ± 0.258, 5.251 ± 0.324, and 6.228 ± 0.423 mg/L, respectively (Table 4.4). Concentrations of selected metals in the rainy season (Table 4.5) were 6.803 ± 0.462, 0.631 ± 0.091, 4.280 ± 0.235, 6.579 ± 0.410, and 2.231 ± 0.131 mg/L, respectively. Concentrations of chromium were above the MAL of 0.05 mg/L throughout the season; during the rainy season, increased precipitation results in higher surface runoff. This runoff can pick up and transport chromium from various sources, including contaminated soils, industrial sites, and urban areas, into the dam. The volume and speed of runoff during

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heavy rains can exacerbate the leaching and transportation of chromium, leading to spikes in its concentration in water bodies.

4.2.2.5 Comparison of selected heavy metals obtained in different seasons.

This study investigated samples from different locations (Dzindi river, Mutale river, Luvuvhu river, and Nandoni dam). Figure 4.1–4.4 show the variation in concentration of selected metals for the dry and rainy seasons. All samples contained As, Cr, Fe, Al, and U in both seasons. According to Dinka et al. (2016), higher concentrations of As, Cr, Al, and U were found in Figure 4.1 during the rainy season due to the leaching of soil erosion from rocks such as limestone, dolomite, calcite, and magnesite contamination from sewage and industrial waste. In Figure 4.2, it was observed that all concentrations were higher in the rainy season. In Mutale river, the concentrations were higher compared with other locations since Mutale river is near the mine, which contributes more pollution to the environment. Figure 4.3 shows a higher concentration of selected metals (As, Cr, Al, and U) during the rainy season. It showed a similar trend of concentration to figure 4.1. Figure 4.4 shows a higher concentration of Cr, Al, and U in the dry season, but As was below the detected limit. Cr was found to be higher in Nandoni dam due to the fact that the majority of the environmental releases of Cr are from industrial sources, particularly from industrial processing and manufacturing of chemicals, minerals, steel, metal plating, leather tanning, textile dyeing, electroplating, cement production, metallurgical, and other works (Nakkeeran et al., 2018; Lian et al., 2019). These industries are creating a huge amount of wastewater, including solid sludge and Cr-bearing waste; for example, tannery effluent is causing severe Cr pollution in the dam (Yoshinaga et al., 2018).

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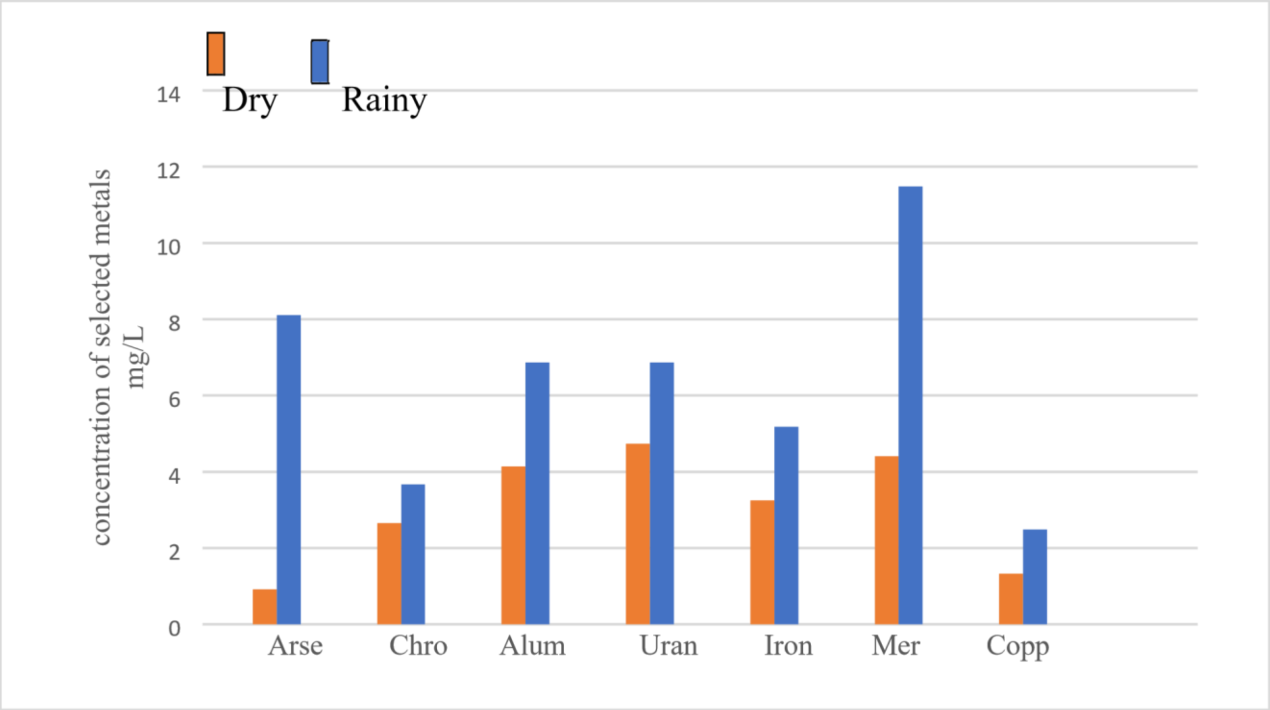

Figure 4.1: variation of selected metals of concentration in dry and rainy season in sample of Dzindi river.

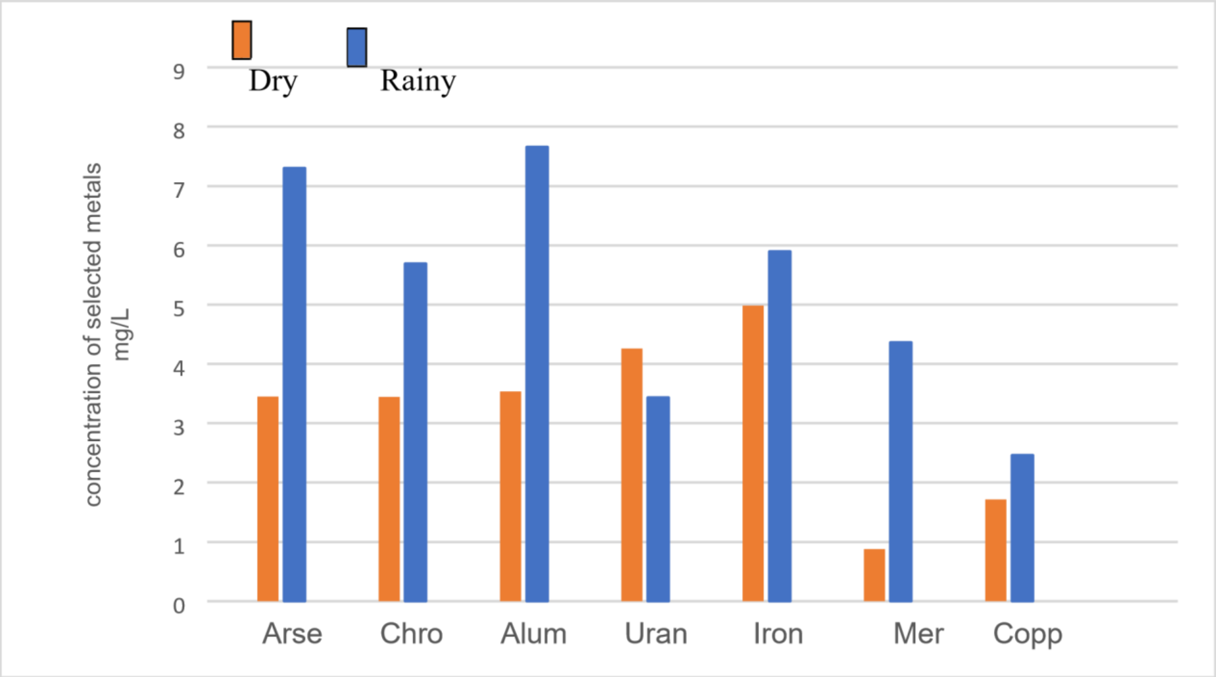

Figure 4.2: variation of selected metals of concentration in dry and rainy season in sample of Mutale river.

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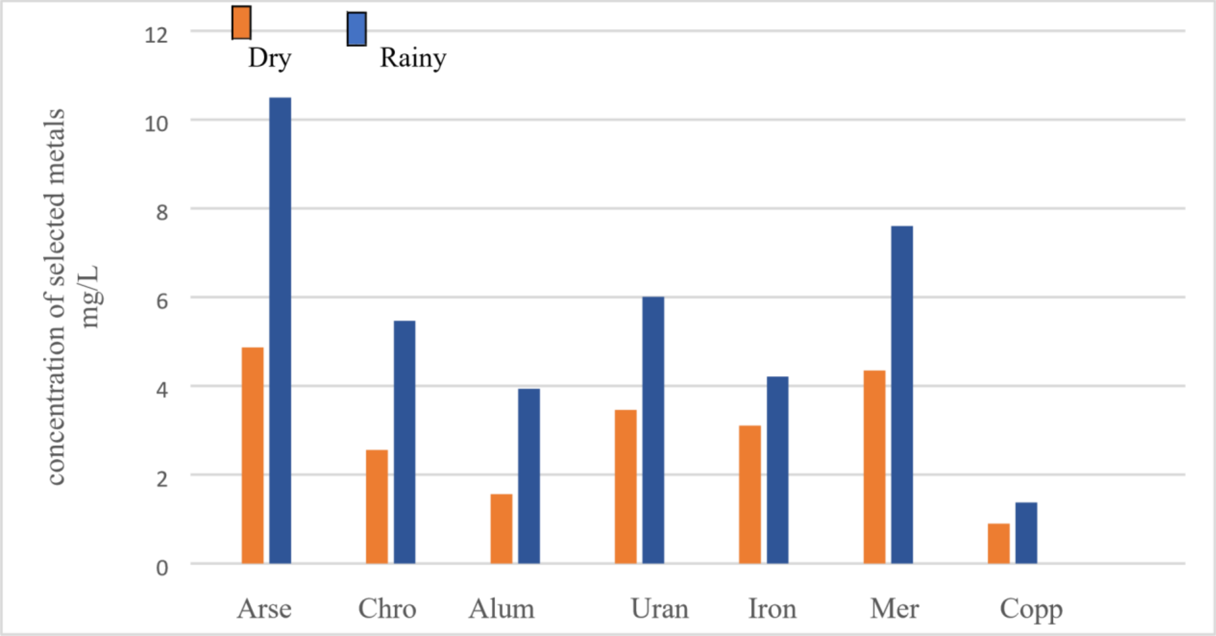

Figure 4.3: variation of selected metals of concentration in dry and rainy season in sample of Luvuvhu river.

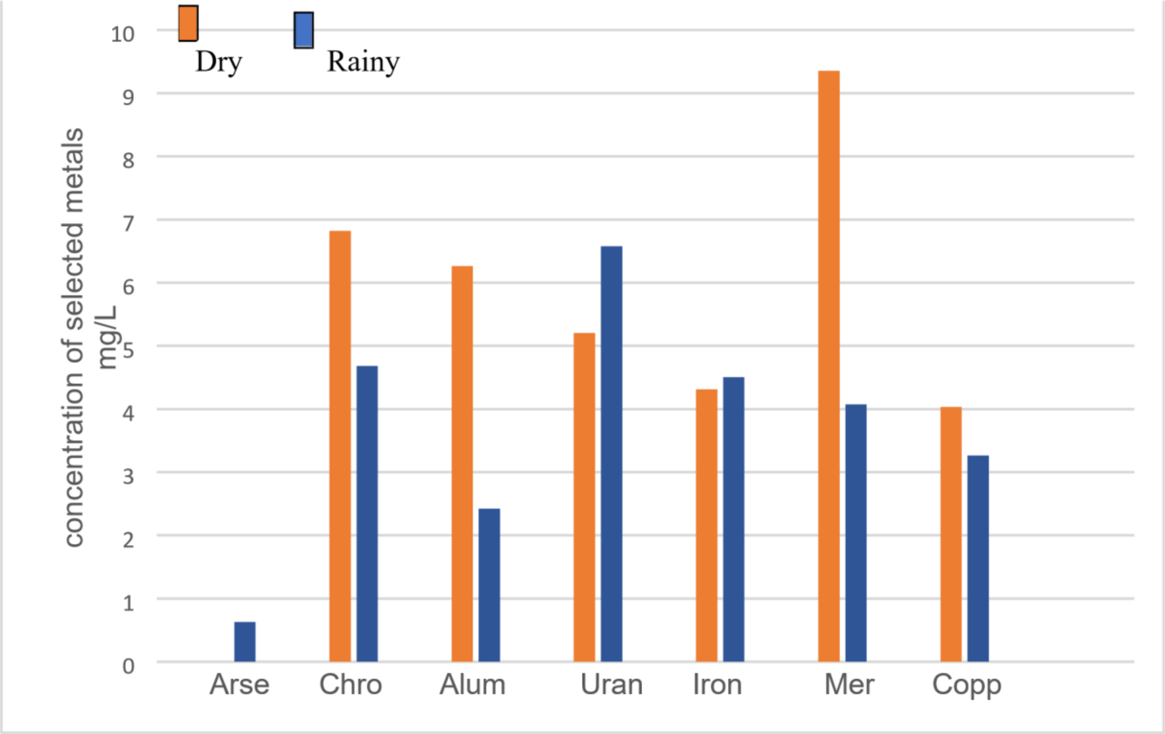

Figure 4.4: variation of selected metals of concentration in dry and rainy season in sample of Nandoni dam.

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4.3. Speciation of chromium using FAAS

Introduction

This chapter presents the findings obtained from the tests and techniques conducted to determine the different forms of chromium using FAAS. The study's primary objective was to determine the various chemical forms of chromium (Cr) in water samples obtained from Mutale river, Dzindi river, Luvuvhu river and Nandoni dam. The aim is to determine the overall content of Cr and Cr (VI) in water samples. Additionally, we will compare the Cr and Cr (VI) levels among all sampling locations.

4.3.1 Calibration curves for the determination of Cr and Cr (VI)

The calibration curves, consisting of five standards and one blank, were created using optimized circumstances. These curves exhibited a high level of linearity, with R^2 values above 0.999. Figure 4.5 presents a calibration curve for measuring the overall concentration of chromium using FAAS. Figure 4.6, on the other hand, depicts the calibration curve specifically for determining chromium concentration (VI) using FAAS.

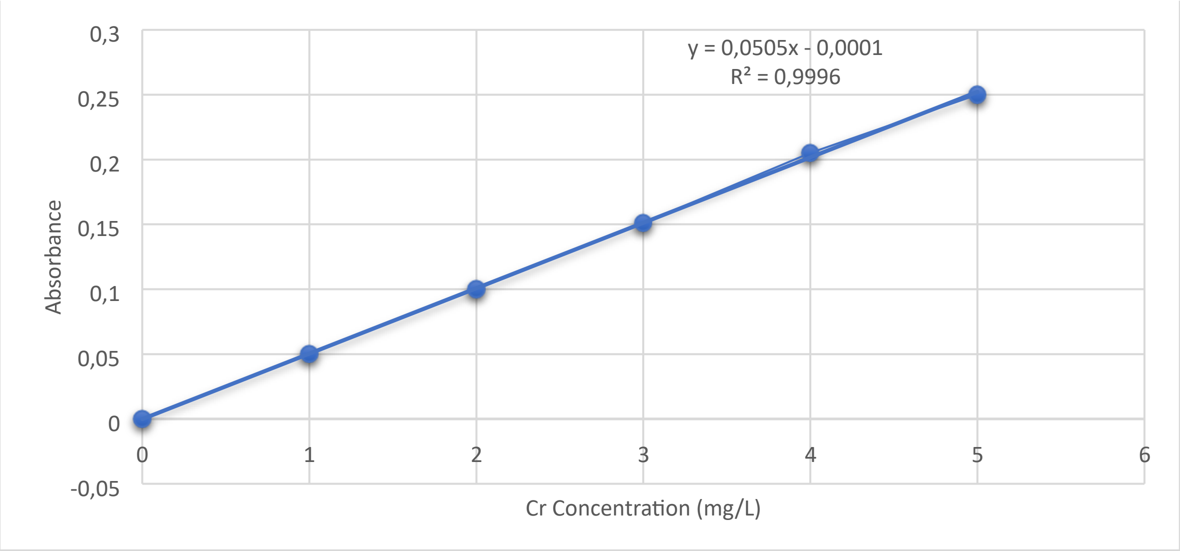

Figure 4.5. Calibration curve obtained for determination of Cr by FAAS

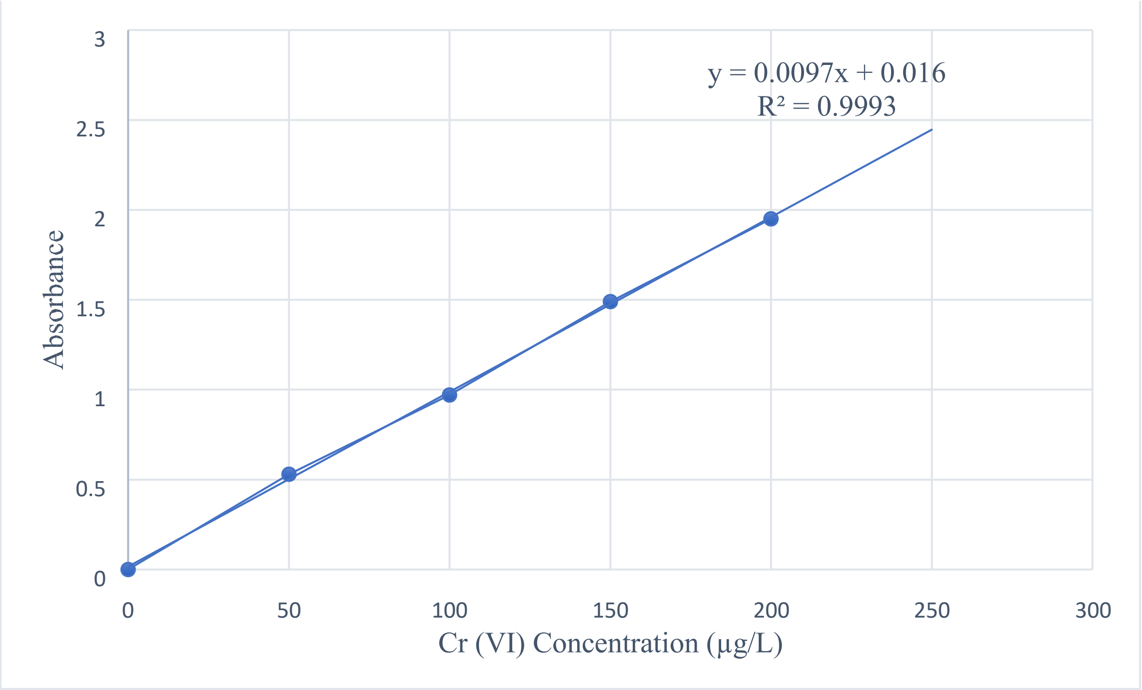

Figure 4.6. Calibration curve obtained for determination of Cr (VI) by FAAS

4.3.2. Determination of Cr in water samples

4.3.2.1. Total Cr concentration in river water samples

Average concentration measured using FAAS ranged from 2.406 to 4.245 µg/L for the dry season and from 3.651 to 6.304 µg/L for the rainy season. The results in Table 4.6 show that they are all within the permissible level for chromium in water. Additionally, concentrations were higher during the rainy season compared to the dry season. Average concentrations of chromium in the water sample for Dzindi river ranged from 2.406 (dry season) to 3.651 (rainy season), Mutale river ranged from 3.531 (dry season) to 4.401 (rainy season), Luvuvhu river ranged from 2.803 (dry season) to 5.013 (rainy season), and Nandoni dam ranged from 4.245 (dry season) to 6.304 µg/L (rainy season).

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During both the dry and rainy seasons, Nandoni dam water samples exhibited greater quantities of chromium concentration. Jayasinghe et al. (2003) used GF-AAS to identify Cr levels ranging from 2.86 µg/L to 8.59 µg/L in river water samples. Results revealed that industrial operations and local and municipal wastes are not primary sources of chromium in water, but it occurs naturally as well. Alam et al. (2003) reported greater Cr concentrations (3 µg/L–13 µg/L), which was found to be similar to the concentration recorded in our study.

In the dry season, the chromium concentration in water samples from the Dzindi, Luvuvhu, and Mutale rivers was below the permissible limit. These concentrations were found in the Tinishu Akaki river in Ethiopia, as reported by Melaku et al. (2005), which ranged from 1.98 µg/L to 19.13 µg/L. However, Barker (2008) found higher total chromium concentrations in the Levubu river, with values of 53.5 µg/L, 57.0 µg/L, and 54.0 µg/L, respectively, which exceeded those observed in the mentioned study.

Table 4.6: Concentration (µg/L) of Cr in water samples collected from Mutale river, Dzindi river, Luvuvhu river and Nandoni dam during dry and rainy seasons.

Sampling site	**Mean Cr concentration** (µg/L)		**Standard guidelines Cr (µg/L)**
	Dry season	Rainy season	
Dzindi River	2.406 ± 0.105	3.651 ± 0.204	50 (WHO, 2017).
Mutale River	3.531 ± 0.324	4.401 ± 0.073	
Luvuvhu River	2.803 ± 0.215	5.013 ± 0.342	
Nandoni Dam	4.245 ± 0.402	6.304 ± 0.431	

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4.3.2.2. Comparison of total Cr levels in water samples from the Dzindi river, Mutale river, Luvuvhu river and Nandoni dam during dry and rainy seasons.

The concentration of chromium (Cr) in the environment can be significantly influenced by both anthropogenic activities and natural seasonal variations, such as the rainy season (run off). Anthropogenic activities, such as industrial discharges, are widely used in industries such as leather tanning, electroplating, stainless steel production, and textile manufacturing. These industries often discharge waste containing Cr (VI), a highly toxic and mobile form of chromium, into water bodies. Industrial effluents containing chromium can contaminate soil and water through direct discharge or improper waste disposal. This leads to elevated chromium levels in nearby rivers, lakes, and groundwater. During the rainy season, events such as increased runoff occur. During the rainy season, increased precipitation results in higher surface runoff. This runoff can pick up and transport chromium from various sources, including contaminated soils, industrial sites, and urban areas, into rivers, lakes, and groundwater systems. The volume and speed of runoff during heavy rains can exacerbate the leaching and transportation of chromium, leading to spikes in its concentration in water bodies.

Over the last several decades, the increased use of Cr in a variety of anthropogenic activities (Gu et al., 2012; Wang et al., 2013; Qiu et al., 2014) has resulted in water pollution. Nandoni dam water tests contained considerably greater quantities of both dry and rainy season contaminants. The Nandoni dam is surrounded by human activities, which are resulting in more Cr in the water. Stainless steel waste dumped in rivers and dams during rainy days might have contributed to an increase in Cr content. Chromium may be included in household trash from numerous synthetic products. When Cr-contaminated wastewater is discharged into rivers, the concentration of Cr rises. Agricultural activities are plentiful along the Nandoni dam as compared to other rivers. Table 4.6 shows a representation of Cr levels in the Nandoni dam, Dzindi river, Luvuvhu river, and Mutale river.

Nandoni dam had a high chromium concentration of 6.304 ± 0.431 µg/L (rainy season) and 4.245 ± 0.402 µg/L (dry season). The Cr concentrations found in the Dzindi river and Luvuvhu river were lower than those found in the Blood diver, Limpopo Province (Mokgohloa C.P., 2019). Edokpayi et al. (2016) found the Cr concentration ranged from 10 µg/L to 590 µg/L in the Mvudi river, which was above the Cr concentration of this study. Mandina and Mugadza (2013) found Cr values ranging from 4.20 µg/L to 8.0

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μg/L in wastewater samples using flame atomic absorption spectrometry (FAAS). The Cr concentrations recorded in this study were equivalent to those discovered in Penang (Alsaffar et al., 2016).

4.3.3 Determination of Cr (III) and Cr (VI) in water samples

Hexavalent chromium increases because of the erosion of natural chromium deposits in the environment. For environmental impact studies, the measurement of Cr (VI) is even more significant. During the dry season, Cr (VI) concentrations ranged from 1.501 ± 0.092 to 3.434 ± 0.138 μg/L for all water sample sites (Table 4.7). Jayashinge et al. (2003) reported that the concentration of Cr (VI) ranged from 1.95 μg/L to 5.65 μg/L using GFAAS. The disparity in Cr (VI) concentrations might be attributed to differences in weather, season, and environmental circumstances. During the dry season, Nandoni dam recorded high hexavalent chromium Cr (VI) concentrations for the dry season (3.434 ± 0.138 μg/L) and for the rainy season (5.819 ± 0.158 μg/L). Therefore, Nandoni dam was found to contain high concentrations of Cr (VI) compared to other sampling sites due to industrial discharges such as stainless-steel production and textile manufacturing, which lead to elevated chromium levels. The Dzindi river was found to have a lower Cr (VI) concentration compared to other sampling sites. Chromium Cr (VI) concentrations of 80 μg/L were found in surface and ground waters utilized for public water supply in Greece's Asopos river (Vasilatos et al., 2008). Water samples from all sampling sites included 21.2 % to 32.7 % Cr (VI) during the dry season and 33.2 % to 45.6 % Cr (VI) during the rainy season. This shows that Cr (VI) was present in comparatively low amounts in comparison to total Cr throughout the dry season. This might be due to erosion and leaching, as rainwater can enhance soil erosion, particularly in areas with loose or disturbed soils due to human activities. Erosion can mobilize chromium particles from the soil and transport them into waterways. Leaching during heavy rains can also increase the dissolution and movement of chromium from the soil into the water, particularly in areas where the soil is saturated with industrial waste. Vasilatos and colleagues (2008) reported a percentage that is greater than observed for this study.

Determination of trivalent chromium, the quantification of Cr (III) was mathematically determined as previous studies by Lestsoalo et al., 2018. The mathematical determination involved the subtraction of Cr (VI) from the total Cr and this is presented in the equation 4.1.

$$[\,Cr\ (III)] = [total\ [Cr]] - [Cr\ (Cr)] \qquad (4.1.)$$

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Where [Cr (III)] is the concentration of Cr (III), [total Cr] is the total concentration of Cr determined in total concentration studies, and [Cr (VI)] is the concentration of Cr (VI). All concentrations were measured in (µg/L). The results of the concentration of Cr (III) of Dzindi river, Mutale river, Luvuvhu river and Nandoni dam were below 50 µg/L of WHO during both dry and rainy seasons. (Table 4.7 and 4.8)

Table 4.7: The concentration (µg/L) of total Cr, Cr (VI) and % Cr (VI) in water samples of in different locations during dry season

Sampling site	Cr (III) (µg/L)	Cr (VI) (µg/L)	Total Cr (µg/L)	% Cr (VI)
Dzindi River	0.905 ± 0.013	1.501 ± 0.092	2.406 ± 0.105	28.4
Mutale River	1.510 ± 0.267	2.021 ±0.057	3.531 ± 0.324	32.7
Luvuvhu River	1.099 ± 0.073	1.704 ± 0.142	2.803 ± 0.215	21.2
Nandoni Dam	0.811 ± 0.264	3.434 ± 0.138	4.245 ± 0.402	31.5

Table 4.8: The concentration (µg/L) of total Cr, Cr (VI) and % Cr (VI) in water samples of in different locations during rainy season

Sampling site	Cr (III) (µg/L)	Cr (VI) (µg/L)	Total Cr (µg/L)	% Cr (VI)
Dzindi River	1.517 ± 0.061	2.134 ± 0.143	3.651 ± 0.204	33.7
Mutale River	0.697 ± 0.098	3.704 ± 0.171	4.401 ± 0.073	39.3
Luvuvhu River	1.512 ± 0.158	3.501 ± 0.184	5.013 ± 0.342	33.2
Nandoni Dam	0.485 ± 0.273	5.819 ± 0.158	6.304 ± 0.431	45.6

When naturally leached Cr levels rise, the hexavalent form will occur. The Cr (VI) concentrations recorded in all test sites (2.134 ± 0.143 to 5.819 ± 0.158 µg/L) (Table 4.8), were below values reported by Loock et al. (2014) in surface water near ferrochromium smelters in South Africa's Bushveld Igneous Complex. The percentage of Cr (VI) obtained in water samples from all sampling locations ranged between 21.2 % and 32.7 % for the dry season and 33.2 % and 45.6 % for the rainy season. This is similar to what Izbicki et al. (2015) reported.

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4.3.4. Comparison of Cr (VI) in water from the Dzindi river, Mutale river, Luvuvhu river and Nandoni dam during both dry and rainy seasons.

Nandoni dam contains a higher concentration of Cr (VI) than other rivers, and due to that, the Luvuvhu river feeds into Nandoni dam. Therefore, Nandoni dam ends up having water containing more Cr concentrations, which leads to higher concentrations and more contamination with Cr (VI). During the dry season, it was 3.434 ± 0.138 µg/L, and during the rainy season, it was 5.819 ± 0.158 µg/L.

In this study, the separation of Cr (VI) was successful using a chomabond-NH_2 column, and the separated chromium Cr (VI) was measured for all sampling locations. According to Wandoyo et al. (2006), the chromium (VI) concentrations ranged from 0.03 to 0.04 mg/L; therefore, they are significantly greater than the current study. The study found that the concentrations of hexavalent chromium (Cr (VI)) in the water samples from the Dzindi river, Luvuvhu river, Mutale river, and Nandoni dam were within the WHO and SA standard guidelines.

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CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

Introduction

This chapter provides a summary of conclusions, recommendations, and future works that have been derived from the results and discussions.

5.1 CONCLUSIONS

The pH of the rivers (Dzindi, Luvuvhu, and Mutale) was virtually neutral (pH 7), although Nandoni dam was alkaline during the dry season, this might due to human activities such as agricultural runoff as it can introduce alkaline substance, like fertilizers into the dam during dry season. During both dry and rainy seasons, pH for all water samples (Tables 4.1 and 4.2) was within WHO (2008), SANS 241 (2006), and Canadian drinking water quality guidelines. Electric conductivity (EC) and total dissolved solids (TDS) levels in all samples were below WHO, SANS, and Canadian drinking water quality guidelines.

Chromium concentrations in water samples were successfully measured using ICP-OES and FAAS. The average concentrations of chromium in water from Dzindi river were 2.406 µg/L (dry season) and 3.651 µg/L (rainy season), Mutale river were 3.531 µg/L (dry season) and 4.401 µg/L (rainy season), Luvuvhu river were 2.803 µg/L (dry season) and 5.013 µg/L (rainy season), and Nandoni dam were 4.245 µg/L (dry season) and 6.304 µg/L (rainy season), respectively. As a supply of chromium was introduced to rivers or dams, concentrations of chromium in water samples increased during the rainy season. Nandoni dam was shown to have significant amounts of Cr throughout the dry and rainy seasons, which is because water in the dam is returned a bit longer compared to river water, where the water is flowing continuously, and also because industrial discharges containing chromium have an effect on water through direct discharge or improper waste disposal. This leads to elevated chromium levels in the dam. It was also observed that the chromium concentrations in water samples at all test sites were below the permissible limit.

The NH_2 column was successful in separating Cr (VI) from Cr (III). The method is simple and accurate. It also provides procedures for sample preparation that are quick, inexpensive, and effective. The SPE methods were preferred because of their simplicity, selectivity, safety, and ease of automation. Results imply that concentrations of Cr (VI) may be successfully detected using alizarin, which binds Cr (III) to prevent oxidation. The results of Cr (VI) in the Dzindi river during the dry season were 1.501 ± 0.092 µg/L, while during the rainy season, it was found to be 2.134 ± 0.143 µg/L. Similarly, values in the Mutale river

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were 2.021 ±0.057 µg/L during the dry season and 3.704 ± 0.171 µg/L during the rainy season. In the Luvuvhu river, the values were 1.704 ± 0.142 µg/L in the dry season and 3.501 ± 0.184 µg/L in the rainy season. In conclusion, the values at Nandoni dam were 5.819 ± 0.158 µg/L during the rainy season and 3.434 ± 0.138 µg/L during the dry season. Hexavalent Cr (VI) was found to have high concentrations after the speciation of chromium, as the concentration of Cr (III) was calculated as the difference between total chromium and Cr (VI), was found to within the WHO permissible limits. Hexavalent chromium (VI) is exceedingly hazardous to humans, plants, and animals. Despite being determined to be high, the Cr (VI) levels were within the WHO and SA standard allowed range. Thus, it can be said that the water from all sampling sites—the Dzindi river, the Mutale river, the Luvuvhu river, and the Nandoni dam—is safe for domestic use because the Cr (VI) levels were determined to be within WHO and SA standards.

5.2 RECOMMENDATIONS

- For successful analyses of chromium (VI) concentrations in water samples, developed SPE method employing Chromabond-NH_2 is recommended.
- Cr speciation in water from all sample sites should be done on a regular basis to disclose the correct amounts of Cr species, particularly harmful Cr (VI). To analyse seasonal fluctuations, can be done during low and high seasons.
- The municipality must raise community awareness and educate residents about the effects of water contamination.
- A significant environmental concern arises from elevated concentrations of TDS, EC, and other relevant parameters; this necessitates urgent attention and appropriate treatment, given that human survival is dependent on water.

5.3 FUTURE WORK

- This study focused on chromium speciation in natural water samples from rivers and dams; therefore, it’s also important to continue with studies on other elements.

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