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Department of Earth Sciences

**Evaluation of water quality, hydrochemical processes, and health risks associated with  
spring water in Thulamela Municipality, Limpopo Province, South Africa**

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requirement of Masters of Earth Sciences (Hydrology and Water Resources)

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## Declaration

I declare that the dissertation '*Evaluation of the water quality, hydrochemical processes and health risks associated with spring water in Thulamela Municipality, Limpopo Province, South Africa*' is my work. The literature used or quoted has been cited in the text and acknowledged using complete references. This dissertation has not been submitted previously to any other institution.

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Signed:

Date: 16 September 2022

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## Dedication

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## Abstract

Groundwater is regarded as one of the most crucial natural resources, globally. In Africa, people have been focusing, extensively, on groundwater, for water supply to meet their daily water needs, especially, in rural areas. This is because the geographic locations of most rural communities are hard to reach, due to them being dispersed and the bad terrain. In South Africa, these conditions have made it difficult and expensive for provision of water services to rural communities. Springs have been widely used for a variety of human needs including recreation, drinking water, domestic water supply and irrigation. In Thulamela Municipality, there are springs located within the Vhembe District in the Limpopo Province, South Africa. This study aimed to evaluate the water quality, potential uses, and health risks associated with spring water in Thulamela Municipality. One hundred and sixty-four water samples were collected from 41 springs between August-September 2020 (dry season) and December-January (wet season) 2020/2021 and analyzed for their physicochemical and microbial characteristics. The analytical data of some physicochemical parameters (pH, Total Dissolved Solids (TDS), Electrical Conductivity, Salinity, Turbidity and Temperature) was determined onsite using Extech multimeter and turbidimeter. All the physiochemical parameters measured complied with the World Health Organisation (WHO) and South African National Standards (SANS) in both seasons, except for turbidity. The concentration of trace elements (Al, V, Mn, Fe, Co, Ni, Cu, Zn, Cr, As, Se, Sr, Mo, Cd, Sn, Sb, Ba, Hg, Pb and Si) were analysed by inductively coupled plasma mass spectrometry (ICP-MS) and major cations (Na, Mg, P, K and Ca) were analysed using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The major and trace metals analysed were recorded in levels below the regulatory limits of WHO and SANS except for Sb in the wet season. Major anions ( $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $NO_2^-$ , Br,  $PO_4^{3-}$  and  $SO_4^{2-}$ ) in the spring samples were analysed using Ion Chromatography (IC). The concentrations of  $F^-$ ,  $Cl^-$ ,  $NO_3^-$ , and  $SO_4^{2-}$  complied with the regulatory limit while  $NO_2^-$ , Br,  $PO_4^{3-}$  exceeded the limits in both seasons. Microbiological parameters (*Total Coliform*, *faecal coliform* and *E. coli*) were tested using Membrane Filtration (MF) method. None of the spring water samples complied with the regulatory guidelines of 0 cfu/100ml set by WHO and SANS, for human consumption. *Total coliform* were recorded in all of the samples, in both seasons. Faecal coliform showed 85.4% and 95.13% presence in the dry and wet seasons whereas *E. coli* detected 34.15% in dry season and 58.53% in the wet season. The Water Quality Index (WQI) was also computed based on parameters: Mn, Fe, Ni, Cu, Cr, Cd, Ba, Pb, Mo and Zn. The WQI in Thulamela Municipality showed 100% and 80.04% for dry and wet seasons, respectively of sampled spring water can be regarded as excellent water quality, whereas and 19.51% for dry and wet seasons, respectively are considered as good water quality. The Piper diagram was

determined by three hydrochemical types, namely, Ca-HCO<sub>3</sub>, mixed Ca-Mg-Cl, and Ca-Cl<sub>2</sub> water types in wet and dry seasons. The dominant water type in dry season and wet seasons were Ca-Mg-Cl and Ca-HCO<sub>3</sub>, respectively. The principal hydrochemical processes shaping the groundwater chemistry are either dilution or mixing. Gibbs plots in all the studied seasons suggested that spring weathering material was the prevailing system controlling the science of the springs at the study area followed by evaporation. Health risks, from assessment of carcinogenic and non- carcinogenic materials, were detected in the water. Hazard Quotation (HQ) and Hazard Index (HI) were lower than 1, in both seasons (wet and dry) for children and adults. Cancer Risks (CR) showed that they were in order of Cr>Ni>Pb>Cd from highest to lowest in both seasons for both adults and children. CR of Pb for adults and child recorded 21.95% (dry), 7.7% (wet) and 21.95% (dry), 4.8% (wet), respectively, in accordance with the recommended guideline of US EPA. 100% of Cr in both seasons for adults and children was recorded, where the sampled spring water exceeded the threshold limit. The level of Cd revealed in the study complied with the limit of CR in all sampled springs for both dry and wet seasons. Ni values of CR showed 100% for both seasons, for adults which complied with the recommended level, while with children, the values exceeded for both seasons. The statistical analysis showed that there was weak or no correlation between studied parameters in both seasons. There was significant difference found in most parameters of the average levels obtained during wet and dry seasons on spring water, such as *total coliform*, *faecal coliform*, temperature, pH, turbidity, Mo , As, Cr, Cu, Ni, Mn, Na ; Mg, Si, P, K , phosphate and nitrite ( $P<0.05$ ). Those that showed no significant difference were *E. coli*, salinity, TDS, EC, Al, Hg, Pb, V , Co, Se, Sr, Sn, Sb , Cd, Fe, Zn, Ba, Cl, sulphate, fluoride, Br, nitrate ( $P>0.05$ ). The Quantitative Microbiological Risk Assessment (QMRA) results showed, the risks of infection per-day results obtained for dry and wet season; these showed that for a child the range was 0 -2.38% (dry) and 0- 2.936% (wet), whereas for adults, the range was 0 - 26.566% (dry) and 0 - 27.459% (wet). There was a relatively high annual risk of infections observed in this study with highest values of 99.58% (child) and 98.80% (adult). The risk of illness values observed showed a range of 0-34.855% (adult) and 0-35 % (child), recorded at S24. This study also presented spatial distribution assessment of water quality to help with better mapping and managing of water quality parameter. The results provide useful data on the suitability of the use of spring water in Thulamela Municipality, hence, provide baseline information of water quality status of the study area. The study recommends that there should be proper treatment of spring water before consumption and increasing public awareness of local communities about spring water and its importance.

**Key words:** *Spring water, Water quality, Health risks, Trace elements, Use of spring water.*

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## Important Acronyms and Abbreviation

$\mu\text{S/cm}$	Micro Siemens per centimetre
AAS	Atomic Absorption Spectroscopy
BDL	Below Detection Level
Ca	Calcium
Cd	Cadmium
CF	Contamination Factor
$\text{Cl}^-$	Chloride
Co	Cobalt
CR	Cancer Risks
CR	Carcinogenic Risk
Cr	Cranium
CSIR	Centre for Scientific Research.
Cu	Copper
$^{\circ}\text{C}$	Degree Celsius
D-R	Dose-Response
DWS	Department of Water and Sanitation
<i>E.coli</i>	Escherichia Coli
EC	Electrical Conductivity
EPA	Environmental Protection Agency
FC	Faecal Coliforms
$\text{F}^-$	Fluoride
Fe	Iron
$\text{HCO}_3^-$	Bicarbonate

HI	Hazard Index
HQ	Hazard Quotient
IC	Ion chromatography
ICP-AES	Inductivity Coupled Plasma- Optical Emission Spectrometry
ICP-MS	Inductively coupled Plasma Mass Spectrometry
ICP-OES	Inductively coupled Plasma-Optical Emission Spectroscopy
IWQM	Integrated Water Quality Management.
IWRM	Integrated Water Recourse Management.
MF	Membrane Filter
Mg	Magnesium
Mg/L	Milligram Per litre
Mn	Manganese
$NO_2^-$	Nitrite
$NO_3^-$	Nitrate
$Na^+$	Sodium
Ni	Nickel
NIST	National Institute of Standards and Technology traceable guidelines
NSF-WQI	National Sanitation Foundation Water Quality Index
NTU	Nephelometric Turbidity Units
NWA	National Water Act
P	Phosphorous
Pb	Lead
QMRA	Quantitative Microbiological Risk assessment
<i>RfD</i>	Reference dose



$SO_4^{2-}$	Sulphate
SANS	South Africa National Standard
SD	Standard Deviation
SDGs	Sustainable Development Goals
SF	Slope Factor
TDS	Total Dissolved Solids
TF	Total Coliform
UNEP	United Nations Environmental Programme
UNICEF	United Nations International Children's Emergency Fund
USEPA	United State Environmental Protection Agency
WHO	World Health Organisations
Zn	Zinc

# CHAPTER ONE

## 1.1 Background

Water is valuable to all living organisms on Earth (WHO, 2011). A spring is a point at which water flows from an aquifer to the Earth's surface (Amanial, 2015); it may be the result of karst topography where surface water has infiltrated the Earth's surface (recharge area), becoming part of the area's groundwater (Dabrowski and de Klerk, 2013). Springs are vital components of the environment and react well to any progressions in the biological systems, hence, they can be regarded as significant hydrogeological indicators (Ibeneme et al., 2013).

Groundwater (particularly springs) is globally known to be a safe, topographically protected, and significant source of drinking water. The relationship between ground and spring water is that, spring water occurs when pressure causes natural flow of groundwater into the Earth Surface (Durowoju et al., 2019). Spring water is impacted indirectly and directly by human activities, globally (Waheed, et al., 2021), therefore, protecting the quality of the water table is a major problem. This has led to several water-related problems associated with drinking water (Machona et al., 2017). The quality of spring water is threatened severely by pollution, agriculture practice, abstraction, microbiological and chemical contamination (Dabrowski and de Klerk, 2013).

The World Health Organisation (WHO)/ United Nations International Children's Emergency Fund (UNICEF) (2019) has estimated that approximately 1.2 billion individuals worldwide do not have access to adequate drinking water sources. Consequently, 2.3 million people die of water-borne diseases (diarrhea, typhoid, and bilharzia) annually, and they are mostly children. Approximately 437 million people are using water from unprotected wells and springs globally (WHO, 2019). In developing countries like Ethiopia, Zambia, South Africa, Uganda, Kenya, Bangladesh, and Mozambique among others, people live in areas where water is scarce (Bloomfield, 2012), therefore, they resort to water sources, such as springs to address their needs. Large parts of the populace, living in non-developed nations are not provided with a sufficient quantity of clean and safe water and are constrained to utilize water sources such as springs, boreholes, rivers, and streams (Mwangi, 2014). Given that the water from springs is mainly used for domestic and agriculture purposes around the world, it is important to understand the quality of such water (CSIRO, 2017). Spring water have been mainly utilized for hygiene purposes, religious ceremonies and social purposes in countries like Japan, Zambia, India, Jordan, Brazil, Crete, Zimbabwe, Kenya, Egypt, Iran, Egypt, South Africa, Harnai, Mozambique, Turkey (Batool et al., 2018; Chauhan et al., 2020; Ahmad et al., 2020, Siminyu et al., 2019; Ameen, 2019). The expansion in spring water

quality deterioration from anthropogenic influence has become unavoidable (Al-Khashman, 2017). Various studies on spring water quality reported that the springs have been contaminated with toxic metals (White *et al.*, 2016, Rao *et al.*, 2017; Ameen *et al.*, 2019; Chauhan *et al.*, 2020; Nnorom *et al.*, 2019; Batool *et al.*, 2018).

Water quality is known to be dynamic in space and time (Vigouroux *et al.*, 2019). Evaluation of water quality is essential as results from them can be used to protect resources for sustainable development, improve drinking water and human health. It is reported that the variety of Spatio-temporal in spring water quality is controlled by the occurrence of hydrogeochemical process at the region of recharge and the interaction of groundwater (Molekoa *et al.*, 2019). An hydrochemical analysis is critical in providing a good understanding of possible changes in the quality of water from springs (Yang, 2016); understanding the nature of groundwater, therefore, is very significant (Chikodzi and Mutowo, 2014). Various studies have shown that the Water Quality Index is important in assessing and classifying water quality for public drinking water (Schiefer *et al.*, 2015; Chadli, 2021; Khan and Qureshi, 2018; Chauhan *et al.*, 2020). There is no current scientific study conducted on the status of spring water at Thulamela Municipality; such an exercise is crucial as majority of people in the area still depend on spring water for drinking, agriculture and domestic purposes. This study, thus, aimed at evaluating spring water quality, its hydrochemical processes, and health risks in Thulamela Municipality, Limpopo Province, South Africa.

## 1.2 Problem statement

Lack of access to adequate quantity of clean and safe water continues to be a worldwide problem that affects around 663 million individuals (WHO/UNICEF, 2015). Springs are a significant source of water as they frequently produce water with high quality which is readily available (Vilane and Dlamini, 2016). Some related studies have shown the presence of toxic metals in spring water capable of impacting negatively on human health (Batool *et al.*, 2018; Anke *et al.*, 2014; AlKhashman, 2017; Barakat *et al.*, 2018). Most people in developing areas in Africa depend on spring water to meet their daily needs (Dutta *et al.*, 2022; Manungufala *et al.*, 2018). The challenge of access to potable water in developing areas may also be due to poverty, weather pattern changes, increase in population, and water contamination from waste disposals, agricultural chemicals, and industries (Ibaishwa and Abaagu, 2018).

Some studies have reported that spring water is used for different domestic purposes, such as drinking, gardening, cooking, and even for irrigation purposes (Tamungang *et al.*, 2016; Durowju *et al.*, 2016). Springs water becomes contaminated when it flows above ground,

allowing animal waste, natural geology, or chemicals to run into the water. This means that people residing in rural areas still depend on unprotected spring water, containing pathogenic organisms or toxic chemicals with undesirable substances.

A study reported by Boumaza et al. (2021) in Algeria revealed that spring water was contaminated by trace elements: magnesium, iron, lead, uranium, lithium, and selenium. The spring water was of poor spring quality with an hazard quotient (HQ) value exceeding 1 and can negatively affect human health, particularly children, causing illnesses such as heart disease, diabetes, kidney failure, and hypertension.

Various studies have established that arsenic contamination of spring water is mostly caused by geology of the area, which could lead to health problems in humans such as vomiting, skin cancer, liver disease, damaged brain, weak immune system, and even death (Biram et al., 2020, Lone et al., 2020; Abeer et al., 2020; Mohammadi et al., 2021; Rehman et al., 2020; Moazeni et al., 2014). Barzegar et al. (2019) reported that in Khoy, Iran, Fe, Mn, Al, Zn, Cr, Co, N complied with the standard guideline levels in spring water except for cadmium and lead which were present in levels exceeding the values.

A high level of fluoride has been reported in spring water of Thulamela Municipality, although, it helps to strengthen teeth and fight against tooth decay, fluoride poses harm to the thyroid, brain, and bone if it exceeds 1.5 mg/L (Enitan-Folami et al., 2020, Edokpayi et al., 2018, Monyai et al., 2016). Microbial contamination (*fecal*, *total coliforms*, and *E. coli*) associated with unprotected and polluted spring water use has been reported to have negative effects on human health (WHO, 2021). Studies conducted by NavabDaneshmand et al. (2018); Khan et al. (2018) and Kayembe et al. (2018) showed the presence of *E. coli* in spring water that people use for drinking, swimming, irrigation and food production; this has led to major health issues like diarrhoea, fever, kidney failure, fatigue, dehydration and urine with blood. A study by Odiyo et al. (2020) showed the presence of fecal coliforms and total coliform due to pit latrines near spring water, and *E. coli* from agriculture and domestic waste activities that have threatened groundwater quality and health of individuals in the surrounding areas. The study further reported cases of diarrhoea and cholera caused by the contaminated water individuals were using for drinking and domestic uses. A study by Taonameso et al. (2020) in the Vhembe district reported a diarrhoea outbreak due to utilization off spring water; people experienced running stomachs, fever, cramps, vomiting after drinking water from springs located near pit latrines and roads which recorded a high level of *fecal* and *total coliform*. It is, therefore, crucial to assess the quality of spring water that people in Thulamela Municipality utilize, to identify the potential health risks associated

with it and determine strategies and measures suitable to improve the water quality and human health.

### **1.3 Motivation**

Water is a crucial natural resource for wildlife, aquatic life, humans, and the environment. Access to safe and clean water is a fundamental human right in South Africa, although, this is not the case in many developing areas. People in rural areas are forced to use alternative sources of water that includes spring water which are not safe. As stated already, spring water is used for various domestic purposes, recreation, irrigation, aquaculture, and drinking (Durowoju *et al.*, 2016, Gunnarsdottir *et al.*, 2016). Unfortunately, spring water quality has not been monitored or assessed to determine, whether it is safe for human use. Drinking-water quality influences human health, hence, there is a need for critical observing and extensive monitoring which is pivotal to protecting the wellbeing of the people (Mofor *et al.*, 2017). Several assessments have been done on spring water quality; findings show that harmful trace elements are deteriorating spring/groundwater water quality (Al-Khashman *et al.*, 2017, Amanial, 2015, Addo *et al.*, 2015; Durowoju *et al.*, 2016). Such studies were limited as they did not present findings on Quantitative Microbiological Risk assessment (QMRA) which is key to estimating the risks associated with the consumption of microbial-contaminated water, hence, this study seeks to close such data gap.

Durowoju *et al.* (2019) performed hydrochemical processes and isotopic study of spring water within Soutpansberg, Limpopo Province, but they did not classify the water using the Water Quality Index. This present study, however, will fill the gap by providing an overall water quality status and suitability of spring water based on several water quality parameters. This study will also help to provide baseline information for relevant stakeholders, such as government, for the management of springs. Previous studies also, did not elucidate on the kind of spring water present in the study area, as well as the interaction between the water and the host rocks. This study area show the hydro geochemistry of the spring water in the study area, and the human health-risk associated with the consumption of trace metals

### **1.4 Objectives**

#### **1.4.1 Main objectives**

The main objective of the study is to evaluate the water quality, potential uses, and potential health risks associated with spring water at Thulamela Municipality.

#### **1.4.2 Specific objectives:**

1. To evaluate the water quality (physical, chemical, and microbiological) of spring water in the study area
2. To investigate the hydro-geochemistry of the springs in the study area
3. To determine the suitability of water using Water Quality Index
4. To determine any human health risk associated with any levels of trace metals and microbial levels recorded in the water.

#### **1.5 Research questions:**

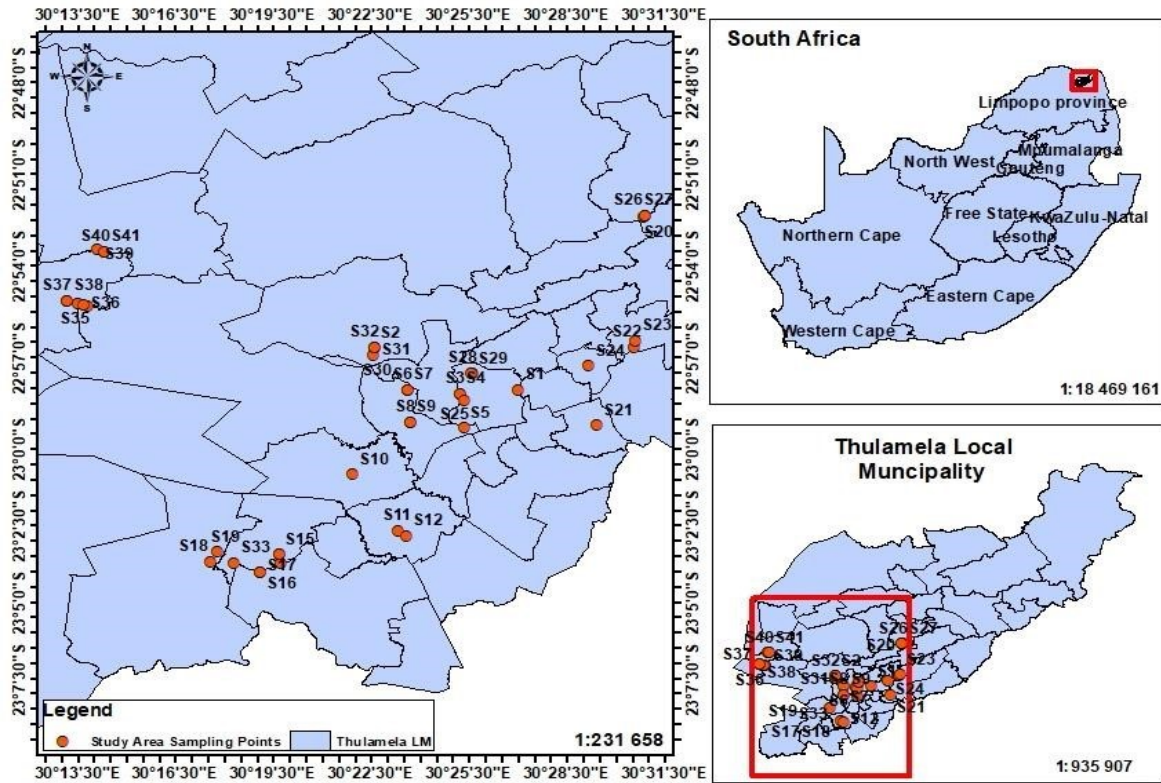
1. What is the current water quality of spring water in the study area?
2. What is the hydro geochemistry of spring water in the study area?
3. What is the water quality status of spring water in the study area?
4. What are the various human health risks associated with any levels of trace metals and microbial levels recorded in the water?

#### **1.6 Study area**

##### **1.6.1 Description of the study area**

Thulamela Municipality (TM) (Figure 1.1) is described as one of the local municipalities - Makhado, Musina, and Collins Chabane - at Vhembe District Municipality. The Kruger National Park (KPN) forms the eastern boundary, while the Municipality shares borders with Makhado Municipality to the southwest and Collins Chabane Municipality to the upper east (Iwara, 2018). Thulamela Municipality is a region covered with many springs due to its terrain.

Thohoyandou its central city is mainly for business, administration, and political activities (Vhembe District Municipality IDP Report, 2018/2019).



**Figure 1.1:** Study areas within Thulamela Local Municipality, Limpopo Province, South Africa

### 1.6.2 Population

The total population of Thulamela Municipality is 602 825 (Netshipise and Semanya, 2022) and those who use springs is estimated to be 5959 (Vhembe District Municipality IDP Report, 2018/2019).

### 1.6.3 Rainfall and Climate

Precipitation plays a crucial role in the development, improvement, and conveyance of vegetation cover; any inconsistency, either excessive or too little precipitation can cause soil erosion and lead to land degradation (WMO, 2015). Thulamela Municipality is exposed to average precipitation because of its topography; the precipitation is greatly influenced by the Orographic of the Drakensberg Mountains linking with the Soutpansberg (Vhembe District Municipality IDP Report, 2018/2019).

As indicated by Nenwiini (2019), the zone near to, or over the Soutpansburg Mountain is classified as a humid segment, receiving 1200 mm of precipitation, while the western and north-western parts receive 500 mm of precipitation. For the most part, Thulamela Municipality is in a semi-dry region and gets mean precipitation of 450 mm (Luvhimbi, 2020). During winter, the area experiences winds (moving from 75 to 100 km/h) (Semanya et al.,

2013). The temperature ranges from 16-38°C during summer and 6-14°C in winter (Sengani et al., 2020).

#### **1.6.4 Geology**

Geology has a strong impact on parameters that are related to floods, for example, vegetation cover, topography, soil types, general hydrology, and soil invasion (Luvhimbi, 2020). Thulamela Municipality has assorted geological compositions; examples are meddling molten, sedimentary, and transformative shakes, particularly in Waterberg and Soutpansberg (Luvhimbi, 2020).

For the most part, the composition of Thulamela Municipality geology is of stone or granite gneiss of the Precambrian age which is alluded to a brilliant gneiss plate (Nethengwe, 2017). Minerals revealed in the study area include clay, rock, marble and conciliatory limestone (Nethengwe, 2017).

#### **1.6.5 Topography**

The region has geology that changes from high mountainous areas (Soutpansberg) to low regions with steep and gentle slopes all around the Municipality (Nethengwe, 2017). The topographic features of Thulamela Municipality influence the atmosphere, for example, the force, intensity, dissemination, and water waste (for example, surface and groundwater). These mountains have a tremendous effect on the climate and atmosphere of the study zone (Enitan-Folami et al., 2020); due to the mountain ranges, some parts of Thulamela Municipality are exposed to high precipitation, leading to flooding in low areas. And therefore?

#### **1.6.6 Vegetation and Landcover**

Vegetation spread plays a significant part in shielding the soil surface from small raindrops, soil aggregate, and decreasing surface run-off. Without the presence of the vegetation cover, the raindrop effect leads to the separation of soil particles and influences crust development (Vhembe District Municipality IDP Report, 2018/2019). Thulamela Municipality has diverse vegetation species that include trees, biomes (savannah), field and woodland, four bioregions, and twenty-three distinctive vegetation types (DEA, 2019). Furthermore, the acacia species are very common in this region.

#### **1.6.7 Hydrology**

Thulamela Municipality is portrayed by both non-perpetual and perpetual rivers that tend to flow during the occurrence of high precipitation occasions and dry out when there is no more precipitation to support them. The region contains a few catchments regions that are



stressed by high demands for water for usage, like farming, human utilization, and mining (Vhembe District Municipality IDP Report, 2013/2014).

## CHAPTER TWO: LITERATURE REVIEW

### 2.1 Introduction

Spring water is any type of that flows onto the outer layer of the earth from beneath (Mansour and Mohammed, 2013). Springs (Figure 2.1) may result from karst geography where water which had penetrated the world's surface, caused the region's groundwater movements through faults and cracks, going from intergranular spaces to caves (Ibeneme et al., 2013; Reda, 2015). Springs are vital components of the habitat which react well to any progressions in natural biological systems, hence can be named significant hydrogeological processes to spring water. In uneven regions, springs are a significant component of groundwater studies (Zelazny, 2017).

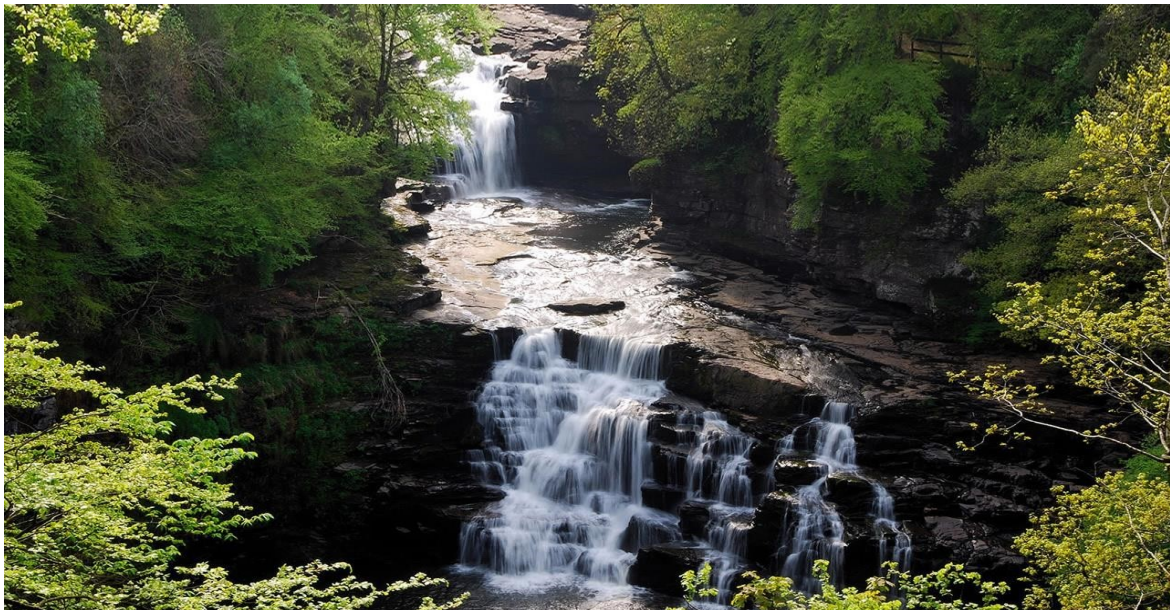


Figure 2.1: Spring (Ibeneme *et al.*, 2013)

Access to spring water is inexpensive as it does not require a pump to transmit the water to the surface; springs are also favourable water sources that produce high-quality water, however, spring water can easily be contaminated (Vilane and Dlamin, 2016).

The major contaminants of spring water are toxic chemicals, natural geology, and pollution from human activities. These contaminants threaten the quality of spring water that is widely used for agriculture, drinking, recreation, and domestic purposes. Furthermore, the use of inadequate amounts of water can result in poor hygiene and cause serious risks to human health (Njoyim, 2016).

Water quality assessment gives the baseline data on water security and since a spring's water quality and purpose for utilization can change with time and different components, continuous monitoring of the water is essential. The list of parameters to be analysed in any water resources differ due to the surrounding conditions of the area (Molekoa et al., 2019). Parameters that are important and considered a need in any spring water quality assessment include microbial, physicochemical parameters, trace elements, and microbiological parameters (WHO, 2011; UNICEF, 2015). Understanding the usage of spring water by the surrounding community of Thulamela Municipality and assessing their water quality is crucial in identifying contaminants to water quality (Ding *et al.*, 2015).

## **2.2 Water Resources at Global and National context**

Water quality is becoming a global concern due to the significant role water plays economically and socially (Du Plessis et al., 2014). Deteriorating spring water quality is a global issue as the human population grows, industrial and agricultural activities expand, and climate change threatens to cause major alterations to the hydrological cycle (UN-Water, 2011).

Developing countries, including Madagascar, Kenya, Burkina Faso, Zimbabwe, Mozambique, Swaziland, and Zambia often have low access to quality water and depend on spring water for a variety of uses, including drinking (Zimmerman *et al.*, 2018). Water provided for direct consumption through ingestion via food, should be of a quality that does not represent a significant risk to human health. WHO/UNICEF (2019) estimated that 1.1 billion people worldwide do not have access to quality drinking water; consequently, 2.2 million water-borne diarrhoeal diseases' deaths occur, annually, mostly among children.

Water use has been increasing worldwide by about 1% per year since the 1980s, driven by socio-economic development, and changing consumption patterns (United Nations World Water Development Report, 2018). Global water demand is expected to continue increasing at a similar rate until 2050, accounting for an increase of 20 to 30% above the current level of water use, mainly due to rising demand in the industrial and domestic sectors (United Nations World Water Development Report, 2018). There are approximately 2.3 billion people residing in developing countries which are experiencing high water stress, and about 3.2 billion people are experiencing severe water scarcity, at least one month of the year. Water stress levels will continue to increase as water demand grows and from the effects of climate change (United Nations World Water Development Report, 2018). The growing population and economies, have increased water demand; increasing

pollution and increased competition for scarce water around the world are also aggravating the situation (Global Water Partnership, 2016).

The water-intensive industrial sectors in modern countries, such as China and Brazil have caused more water withdrawals and produced a lot of wastewater simultaneously; these have possibly polluted drinking water sources, streams, and springs (Grady et al., 2014). Grady et al. (2014) showed that due to high practices of industries, countries, like Malawi was presented with human health harm due to the use of water that was contaminated. In South Africa, poor water quality has been attributed to frequent drought occurrences (Meissner *et al*, 2019). Certain parts of South Africa are faced with growing water demands and insufficient potable water sources (Pegram and Eaglin, 2011; Haigh *et al.*, 2010).

People's modern practices are putting increasing pressure on water resources, and places like, South Africa has surpassed its accessibility to water (Mukheibir and Sparks, 2019; Pitman, 2017). There are also developing concerns that environmental change presents further difficulties in precipitation pattern, like in Cape town (Mukheibir and Sparks, 2019; Galvin et.al., 2015). Drought plays a major role in water deficiencies.

Furthermore, it has been established that water from accessible sources has declined because of expanded contamination brought by transfer of waste, industry, urbanization, mining, and agribusiness exercises from close-by ranches, particularly, in Limpopo, KwaZulu-Natal and Mpumalanga (Musingafi and Tom, 2013). Gumede and Dipholo's (2014) study identified significant government issues in an investigation that focused on New Public Management in South Africa. Sectoral limits, absence of coordination, divided duties, and irregularities among administrative structures have been noted as complexities in water resource management (Haigh et al., 2010; Meissner et al., 2019). The difficulties in water management has brought an urgency for water governance change as poor services are perceived as one of the causes of the current water crisis (Siebrits et al., 2016; Jankielsohn, 2018; Meissner, 2019).

South Africa is one of the countries within the Sub-Saharan region that responded to the water crisis by introducing the National Water Act (NWA) Act No. 36 of 1998 to promote an integrated and decentralized management approach (Walter and Ron, 2011). Numerous areas, including Thulamela Municipality do not have an ideal or transitional level of access to adequate water supply. Springwater has progressively turned into the main source of drinking water, particularly, for rural communities (Gregory, 1996). The first requirement is to improve access to water supplies to guarantee that at essential access is accomplished.

The enhancements in water resources management and access to spring water supply and sanitation services are fundamental to both economic and social areas, such that no population is left behind when it comes to the multiple benefits and opportunities that spring water provides (Musingafi and Tom, 2013). This current investigation seeks to evaluate water quality, hydrochemical processes, and health risks associated with spring water in Thulamela Municipality.

### 2.3 Occurrences of Spring Water

Groundwater is one of the most significant sources of water worldwide, particularly for both developing and developed countries around Africa (Jason et al., 2010). Groundwater exists in the pore spaces and penetrates the rocks and sediments underneath the earth's surface. It begins as precipitation or snow and afterward travels through the soil and rock into the groundwater framework, then advances back to the surface as streams, lakes, or sea (Won et al., 2015; Lyu et al., 2020; Ma et al., 2015; Adimalla and Li, 2019). Groundwater underneath the world's surface is typically limited to depths around 750 m. The volume of groundwater is comparable to a 55-meter-thick layer spread out over the whole surface of the earth (Evaristo et al., 2015).

There are four types of geological formations (Won et al., 2015):

*Aquifers*: how much water a material can hold relies on its porosity. In hydrology, it is determined as a rock layer that can hold water and releases it (Won et al., 2015). The stone contains water-occupied pore spaces, and when the spaces are filled, the water can move through the framework of the rock. A spring can, additionally be known as a 'water-bearing layer' (Gleeson et al., 2012).

*Aquitard*: water is penetrable, partly, in this geologic formation; water is transmitted at a moderate rate (slow) and the yield is inadequate. Pumping in a well is impossible, due, for instance, in the formation of sand in clay (Won et al., 2015).

*Aquiclude*: the flow of water rate is impermeable in this geological material (Won et al., 2015). There is the presence of a high quantity of water in it, yet it does not allow water to pass through it and it cannot yield water either. This is a direct result of its low porosity; rock, clay, or shale are genuine illustration of Aquicludes. They are described as having great water storage capacity. (Werner and Robinson, 2018).

*Aquifuge*: an impermeable geological formation that does not have pores that are connected nor permeable, therefore, water cannot be stored nor passed through it; an example is a rock that is compacted (Werner and Robinson, 2018).

## 2.4 Types of springs

A spring is situated on a slope or incline or low region. As the water flows, it picks minerals potentially from rocks; spring water flowing is regularly sold as mineral water. It is a component of the hydrosphere (Burt *et al.*, 2017). Springs are the basic wellspring of water supply in most rural locations, including Thulamela Municipality. Improving access to safe drinking water is of significant advantage to human wellbeing (WHO, 2011).

A spring is an effect of karst geography where there is infiltration of water surface (recharge zone); this is essential for groundwater (Burt *et al.*, 2017). The water on the ground then goes through faults and openings from intergranular spaces to enormous caves. The water below the surface rises out as a karst spring (Burt *et al.*, 2017).

The force of the spring water can be the consequence of the energized zone of the water table on a higher level than the outlet. Springwater compelled to the surface by raised sources are artesian wells. This is possible regardless of whether the outlet is a cave of (91m) 300-foot-profound. For this situation, the cavern is utilized like a hose, by the higher raised zone of the ground causing the water to exit through the lower opening (Laafou and Abdallaoui, 2014).

Non-artesian springs may fundamentally move through the earth from high height to a lower one and exit as a spring, using the ground as a lined waste. Various springs are the aftereffect of strain from an underground source to the earth, as a volcanic activity (Laafou and Abdallaoui, 2014). The groundwater continually separates to become vulnerable bedrock, for instance, limestone and dolomite, making tremendous sinkhole systems.

There are five types of springs flow: *gravity spring, seepage spring, tubular spring, fracture spring, and artesian springs*

**2.4.1 Seepage or filtration spring** - these springs are known to have low flow rates in which the source water is filtered through porous earth. Groundwater leaks out onto the surface, seepage springs gradually let water out through soil or rock that is loose and are frequently found in low valleys (Cantonati *et al.*, 2012).

**2.4.2 Tubular springs** - The water flows from underground caverns. These springs occur in underground cave frameworks, which take after underground interstates. These cylinders, or channels, are made of limestone, and as water travels through this kind of rock, it breaks down some of it. Tubular springs are probably the biggest springs on earth, although, sometimes their tubes can be extremely small, to the point that you cannot see them (Kresic, 2010).

**2.4.3 Gravity spring** - The water gets pulled down through the ground until it achieves a layer it cannot pass through. From there, it begins to flow horizontally until it achieves an opening and water turns out as a spring; these are found along slopes and cliffs (Cantonati *et al.*, 2012).

**2.4.4 Fracture springs** - They are released from joints, faults, or gaps in the earth; springs have pursued the characteristics of voids in the bedrock. Spring discharge is dictated by its recharge zone (Cantonati *et al.*, 2012). Components that influence the revive zone include the area where the groundwater is determined, measurement of the rainfall and the outlet of the spring size. Water flows into the underground framework from numerous sources including porous earth and holes. Human activities may also influence a spring's water release through the elimination of groundwater; this decreases the water quantity of a spring hence, diminishes the volume (Angelo *et al.*, 2017).

## 2.5 Uses of Springs Water

Table 2.1: Global coverage of spring water use

Studies-reviewed uses of spring water	Area/country	References
Rural communities resort to sources such as spring water for agriculture, drinking water and livestock.	Nepal	Chapagain et al., 2017 ; Gurung et al., 2019
For drinking, washing, irrigation, and livestock use	Iran	Thapa et al., 2020
For drinking, agricultural, and industrial activities, as well as other domestic purposes	Ethiopia	Amanial et al., 2015
For domestic needs which include drinking, bathing, small public buildings and cleaning for residential and institutional premises	Zimbabwe	Machona et al., 2017 ; Chikodzi et al., 2020.
Drinking and irrigation mills	Western Asia	Dumaru et al., 2021
Domestic, recreational, industrial, and agricultural purposes	Central West Bank, Palestine	Ghanemet al., 2021
Domestic and recreational purposes	Siloam, Limpopo Province Soutpansberg, Limpopo Province, South Africa	Durowoju et al., 2016 ; Durowoju et al., 2019
For power generation and heating systems as they have geothermal energy	New York city	Lund et al., 2018
Farms, minor industrial purposes agriculture, various heating systems, greenhouses	Australia	Guðnason et al., 2015
Recreational, religious activities, power generation, bathing, and drinking	Eastern Cape Province of South Africa	Ncube et al., 2020
Drinking, cattle production, agriculture, forestry, generation of electricity and fisheries	Barwari Bala, Duhok, Kurdistan Region, Iraq	Ameen et al., 2019
Electricity generation, drinking, domestic purposes, irrigation and mills.	Ramallah area / West Bank.	Shalash and Ghanem, 2018
Irrigation, recreational activities fishing, swimming, and domestic use	Outer Himalaya, India	Ansari et al., 2019
Drinking water supply and livestock	Tuscan Region of Italy	Ghezzi et al., 2019
For ecological, cultural, recreational and domestic purposes	Osona, NE Spain	Boy-Roura et al., 2018
For domestic, tourism, drinking, and domestic uses	Eastern Cape, Republic of South Africa	Faniran et al., 2019

Domestic and irrigation purposes	Siloam Village, Limpopo Province, South Africa	Odiyo, and Makungo, 2012.

## 2.6 Health risks associated with contaminants in spring water

The human health is closely associated with the quality of water they use. Currently, vast water quality resources are threatened and deteriorated in different countries (Fallahzadeh et al., 2018). Population increase is one of the cause that has led to an increase in waste generation which could potentially contaminate spring water. Studies have shown that the presence of contaminants in spring water can lead to adverse health effects (Table 2.2) (Abed and Alwakeel. (2017); Chauhan et al. (2020); Onipe et al. (2020); Skalnaya and Skalny (2018).

Table: 2.2 Health risks associated with concentration of trace elements in water

Type of Trace element	Reported cases of spring water contamination	Health Risk associated with spring water use	Area/ Region/Province	Reference



<p><i>Fluoride</i></p>	<p>The study area has reported dominance of Fluorite mineral presence in sedimentary rocks and igneous, although, dilution from rainwater also had had an impact.</p> <p>Another study showed a high level of Fluoride from weathering, geographical factors, reactions from ion exchange, and subsurface pollutants draining.</p> <p>The low rate of dilution of groundwater.</p> <p>Agricultural activities</p>	<p>Mottled teeth. Occurrence of fluorosis</p> <p>Fluorosis on animal and human</p> <p>Dental and skeletal fluorosis</p>	<p>Siloam, South Africa</p> <p>India</p> <p>Ethiopia</p>	<p>Odiyo and Makungo et al., 2012; Durowoju et al., 2019</p> <p>Mukherjee and Singh, 2018</p> <p>Mwiathi et al., 2022</p>
<p><i>Arsenic</i></p>	<p>Rock water interaction zone</p>	<p>Vomiting, hypertension, and kidney failure</p>	<p>Pakistan</p>	<p>Shahid et al., 2018</p>

	<p>Industrial waste, smelting copper</p> <p>Sediment-water interactions</p>	<p>Cancer and diarrhoea</p> <p>Cancer risk, stomach cramps</p> <p>Cardiovascular diseases, diabetes, renal system ill effects, high blood pressure</p>	<p>Tshipise and Siloam, South Africa</p> <p>India</p> <p>China</p>	<p>Durowoju et al., 2019</p> <p>Mridha et al., 2022</p> <p>Zhang et al., 2022</p>
<i>Nickel (Ni)</i>	<p>Surface runoff, surface treatment industries</p> <p>Mining, and refining</p> <p>Weathering of soils and rocks</p>	<p>Damage to some internal organs,</p> <p>Cancer</p> <p>Cellular damage, allergy, and lung fibrosis.</p> <p>kidney diseases, cardiovascular</p>	<p>Nigeria</p> <p>Northern China</p> <p>Limpopo Province, South Africa</p>	<p>Adeyemi and Ojekunle, 2021</p> <p>Chen et al., 2020</p> <p>Ricolfi et al., 2020</p>
<i>Copper</i>	<p>Industrial and domestic waste</p> <p>Agricultural runoffs and industrial waste</p> <p>Leaching from sediments and rocks</p>	<p>Anaemia, vomiting, diarrhoea</p> <p>Abdominal pain</p> <p>Damaged lungs and kidneys, loss of strength</p> <p>Lung, dermatitis, and nasal cancer</p>	<p>Iran'</p> <p>Italy</p> <p>Bhojpur District, Bihar State, India</p> <p>Thulamela Municipality, South Africa</p>	<p>Saleh et al., 2019</p> <p>Tiwari et al., 2021</p> <p>Chakraborti et al., 2016</p> <p>Luvhimbi, N., 2020; Genchi et al., 2020</p>

<i>Cadmium (Cd)</i>	Coal and other fossil fuel  Sewage treatment plant and municipal waste	kidney damage and hypertension  Organ and system toxicity, cardiovascular and peripheral nerves.	Thulamela Municipality, South Africa  Muledane area, South Africa	Luvhimbi et al., 2020  Edokpayi et al., 2018
	hazardous waste, mining, industrial wastewater, seepage from waste	Formation of kidney stones and dysfunction of the renal tubular	Jamaica, China, Korea,	Liu et al 2017 ; Hajeb et al., 2015;
<i>Lead (Pb)</i>	Industry, mining, plumbing, gasoline and coal  Plumbing corrosion, inappropriate municipal water treatment	Anaemia, impaired hearing, Lower IQ  Seizures, Hyperactivity	Nigeria, India and Egypt  Ghana and KwaZulu-Natal, South Africa	Adeyemi and Ojekunle, 2021; Raja et al., 2021 ; Salman et al., 2019  Doyi et al., 2018 ;  Mthembu et al., 2021
<i>Chromium (Cr)</i>	Industrial discharge, Mineral weathering and mining waste	Reactions and allergies, e.g skin rash, and nose bleeds	Siloam and Tshipise, South Africa	Olivier et al., 2011 ; Durowaju et., 2015; Skalnaya and Skalny, 2018

## 2.7 Factors affecting quality of spring water

### 2.7.1. Natural factors

Natural water bodies, for example, lakes, springs, streams and groundwater need to contain water of good quality since they are the main water sources on which life depends

(Prathumratana *et al.*, 2018). Natural processes prompting changes in water quality involves weathering of rocks, evapotranspiration, deposition because of wind, filtering or leaching from soil, run-offs due to hydrological variables, and natural procedures in the oceanic condition (Khatri and Tyagi, 2015). These natural processes cause variation in the pH of the water, phosphorus stacking, increment in fluoride substance and high concentration of sulfates (Prathumratana *et al.*, 2018). Figure 2.2 represents some of the natural effects on spring water.

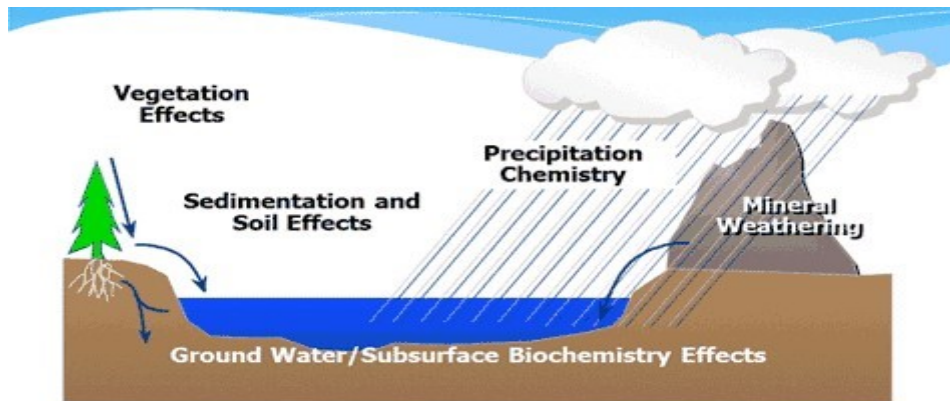


Figure 2.2: Natural sources (Khatri and Tyagi, 2015)

Aspects of water pollution due to natural causes (Khatri and Tyagi., 2015):

1. Increase of sediments in spring water from vegetation and riparian disturbance
2. Potassium from minerals in rock (muscovite).
3. Interaction of rock water (primary source) of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in water underground.
4. Sodium in groundwater from granite rocks.
5. Fluoride occurs naturally in water due to run-off from enduring and fluoride-containing rock weathering and soils filtered to the groundwater.
6. Natural sources from chloride, for example, precipitation, the disintegration of liquid incorporations, and chloride-bearing minerals.
7. Atmospheric deposition of nitrate.

Dilution of substances brings changes in spring water quality. Low spring-flow rates tend to have an impact on the quality of water when there is a rise in temperature and dissolving of substance concentration (Van Vliet and Zwolsman, 2016). Dry season cycles may influence

water quality as they induce decay and flushing of natural waste into streams; water sources may be impacted by drought (Zwolsman and van Bokhoven 2017; Evans et al., 2015).

An increase in water temperature affects chemical nature of spring water, such as an increase in pH level. Seasonal varieties in surface run-offs, rainfall, interflow, groundwater flow, and pumped inflows and outflows have a significant effect on spring water discharge and subsequently on the concentration of pollutants in the water (Smedley and Kinniburgh, 2018).

Dissolved matters affect the proper functioning of aquatic cycle and environments from factors like, acidity, transportation of trace elements, the absorbance of light and photochemistry and supplements of nutrients (D’Odorico et al., 2019). The primary source of disintegrated natural matter in spring waters is soil leaching. Phosphate stacking exportation lead to high precipitation, which will increase environmental change and subsequently affect lakes (Mooij et al., 2015). Many rocks and minerals found in in the world, for example, fluorospar, cyolite, and fluorapatite (Jagtap et al., 2012), contain fluoride (Onipe et al., 2020; Loganathan et al., 2016) which can be released by rainwater and natural weathering, causing pollution of spring water (Mandinic et al., 2020).

### 2.7.2 Anthropogenic factors affecting spring water

Anthropogenic elements affect spring water because of practices like, irrigation, industries, excrements, pesticides, animal-farming exercises, deforestation of woods, contamination due to modern effluents and home sewage, mining, and sporting events (Figure 2.3). These anthropogenic activities cause increased values of metals, mercury, coliforms, and supplement loads in spring sites water (Khatri and Tyagi, 2015).

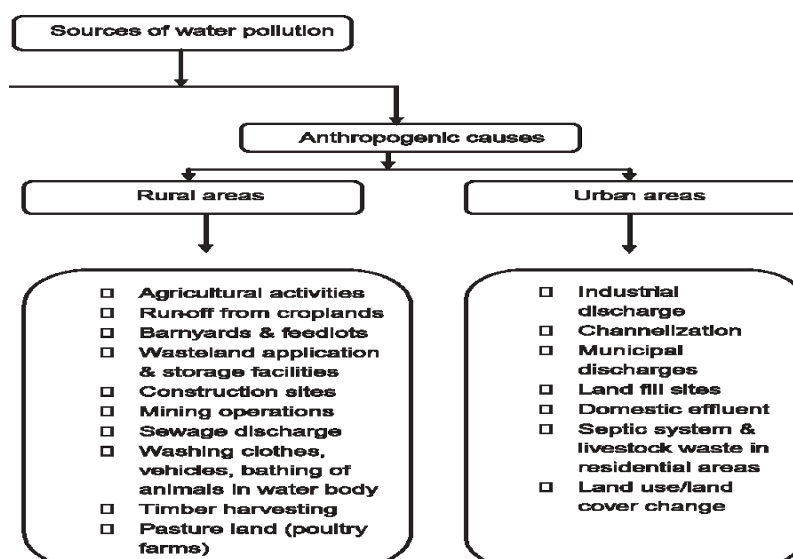


Figure 2.3: Anthropogenic sources affecting water quality of springs in both rural and urban areas (Khatri and Tyagi, 2015)

## 2.8 Previous studies of Quality of spring water

### 2.8.1 Microbial in springs water

#### *i. E. coli*

Since the 1980s, *E. coli* has been used extensively as an indicator of faecal contamination in water and its treatment purposes (Carrero-colon et al., 2011; White et al., 2021). The contamination of spring water can be due to the use of manure, open defecation, leaking of waste, sewage discharges, water draining, and overflow due to storms (Liaquat et al., 2019; Adamou et al., 2020; Islam et al., 2017). A microbiological value showed that the *E. coli*, for Mhlambanyoni spring water, for a studied season (dry and wet) had a concentration of 240.3 counts/100 ml and 844 counts/100 ml, respectively at Sigombeni, Swaziland (Vilane and Dlamini, 2016). A study reported by Barakat et al., (2020) showed that the *E. coli* results exceeded the standard limit of the WHO range of (9-96 CFU/100 ml). Another study conducted by Roslev and Bukh, (2015), showed that waste from animals and sewage discharge was the main source of *E. coli* presence in spring water. Enitan-Folami et al. (2018) recorded a high load of *E. coli* with values of  $2.0 \times 10^1 - 4.6 \times 10^3$  cfu/100 ml for wet season and  $0.0 - 7.0 \times 10^2$  cfu/100 ml for dry season.

#### *ii. Total Coliform*

Total coliforms are considered a useful indicator of other pathogens in drinking water (Sarfraz et al., 2018; Sinha et al., 2017). Total coliform pathogens normally occur in both natural and sewage waters. These microorganisms are discharged from the dung/faeces of people and animals; numerous coliforms are heterotrophic and can increase in water and soil (O'Toole et al., 2012; WHO, 2011). A study by Roslev and Bukh et al. (2015) revealed that total coliforms were 2402 cfu/100 ml for dry season and 5475 cfu/100 ml for the wet season. Furthermore, Egbueri's (2019) study showed that the concentration of total coliform in spring water exceeded the threshold of WHO of 0 cfu/100 ml with a range from 1 to 7 cfu/ml. A study conducted by Yasin et al., (2015) showed coliform from unprotected water sources - total coliforms and faecal coliforms (80%) positive and 100% on Total coliform. A study conducted by Sarfraz et al. (2018) in Pakistan revealed that total coliforms were significantly present in groundwater with minimum and maximum of 62 and 84%, respectively; Siminyu

et al. (2019) reported that total coliforms recorded was high in most of the studied water springs.

### *iii. Faecal Coliform*

The presence of faecal contamination is an indicator that a potential health risk exists for individuals exposed to this water (Liu et al., 2018; Aguayo et al., 2016). Studies have indicated that contamination of spring water due to faecal coliform may be as a result of the adjustment of various land use, domestic sewage, seasonal variation and animal waste (De Giglio et al., 2016; Li et al., 2015; Sinha et al., 2017). High amounts of faecal coliform were detected in a study by Farouq et al. (2018); the results indicated that all of ten sampling locations showed the presence of faecal coliform ranging from 10.70 -29.00 cfu/100ml, in Nigeria. A study was done by Muzenda et al., (2019) where faecal coliform was detected with a level of

$77 \pm 36$  cfu/100 mL in Zimbabwe. An investigation conducted by Barakat et al., (2018) showed that concentrations recorded for total coliforms ranged between, 180 -290 cfu/100ml. EnitanFolami et al., (2018) in their study reported the presence of faecal coliforms in the Muledane community with a range of  $2.0 \times 10^1$  – $6.0 \times 10^2$  cfu/100 ml for wet season and  $0.0$  –  $1.0 \times 10^1$  cfu/100 ml for dry season.

## **2.8.2 Physical characteristics of spring water**

### **i. Total Dissolved Solids (TDS) and Electrical Conductivity (EC)**

Measurement can be done of all inorganic and natural substances contained in the spring water in an ionized suspended structure and molecular (Qureshi et al., 2021). Some studies reported that high values of EC are from horticulture exercises and residential run-off into spring water (Tiwari et al., 2020; Enithan-Folani et al., 2018). Water with high values of TDS and EC can have negative effects on human health, such as causing gastrointestinal irritation and kidney problems (Liu et al., 2019). The results from Heidarinejad et al., (2018) showed that the concentration of TDS fell within a range of 124.80 mg/L to 162.20 mg/L. A study by Barakat et al., (2018) reported on cases that were within the standard guidelines, with a range of between 420 and 701  $\mu$ S/cm with a mean value of 574.9  $\mu$ S/cm. Other studies showed the presence of TD and EC in spring water with values of electrical conductivity of 168–

3170  $\mu$ S/cm and 50–1550 mg/L respectively (Adimalla and Taloor, 2020); Mahmud et al. (2020) reported 1650  $\mu$ S/cm of EC and 1188.7 mg/l for TDS. Groundwater samples from a

study presented by Tiwari et al. (2020) showed that (EC) varied from 190 to 442 mS/cm and the highest values of TDS was found at 335 mg/L value in the study area.

The nature of EC in water decides whether water is drinkable or not; this can be upheld by an investigation Durowoju et al., (2019).

$$\text{TDS (mg/l)} = 0.67 * \text{EC } (\mu\text{S/cm}) \text{ (Hayashi, 2004)}$$

#### ii. Temperature

Temperature plays a vital part in quality and sources of water as it concerns reactions of chemicals and rates of metabolic processes of organics; it is consequently a controlling variable of amphibian species circulation (Miyakoshi et al., 2020). Exercises related to temperature change, include, sources abstraction, land-use change, warm effluents from power generation, environmental change and modern cycles. Bouteraa et al., (2019), presented that the temperature of the spring water samples may vary from 13 to 19 °C. Durowoju et al. (2019) recorded temperature of geothermal springs, which ranged from 41 °C to 49 °C (hot) and 53 °C to 69 °C (scalding waters), whereas Onipe et al., (2020) reported temperature of groundwater at values of 45 °C and 48°C. Odiyo et al. (2020) recorded a range of temperature from 22.1 to 27.6 °C and 22.1 to 27.6 °C. Their study further stated that high temperatures have negative effects on spring water quality as it enhances microorganisms that lead to odour, taste, color, and corrosion problems.

iii. Turbidity

Turbidity is significant for water quality parameters because it indicates whether groundwater may be under a negative influence or not. The presence of high turbidity from suspended solids in spring water is brought about by a possibly polluted spring water within the aquifer. Most studies have stated that high levels of turbidity can be caused by heavy rain leading to soil run-offs, erosion and untreated waste from sewage (Muzenda et al., 2019; Qureshi et al., 2021). Turbidity in drinking water is aesthetically not accepted and can also negatively impact human health and aquatic life; turbidity in water can obstruct fish gills, diminishing its protection from different diseases, low development rates, negatively influencing egg and larval developing, and influencing the effectiveness of fish-catching strategy (Batool et al., 2018; Raimi et al, 2018). High Turbidity in water can also increase the cost of water treatment for various uses (Kiprono, 2017). Results obtained by Makungo et al., (2018) showed samples that fell within a range of 0.00 to 25.91 NTU. Another study by Sengani and Zvarivadza (2018) showed that turbidity of all studied boreholes was found in the range of 1–5 NTU which were within the required standard.

#### iv. pH



The pH determines the concentration of Hydrogen ions in water (Sorlini et al., 2016). It influences other water parameters, and it tends to be crucial because it determines which chemical compounds are available and their relative toxicity in the aquatic environment (Abel, 2017). A high pH can influence water potability; it can be brought by calcium carbonate from limestone rocks. The concentration of oxygen in water has a direct relationship with pH, as it increases. A low pH level helps to corrode or disintegrate metals and different substances; it can also diminish the number of fish eggs, fish irritation, insects, aquatic gills, and harming of membranes. pH ranging from 6.5 to 8.5 is determined as a safe range for drinking water and living organisms (WHO, 2011). The results obtained by Makungo et al., (2018) showed a range of 7.26 to 9.29, whereas Enitan-Folami et al. (2018) study reported ranges from 6.04-7.17 which fell within the recommended limit.

## **2.9 Quantitative Microbial Risk Assessment (QMRA)**

Quantitative Microbial Risk Assessment (QMRA) framework has been applied by different studies to survey the potential microbial *wellbeing* related to uses of spring water, such as drinking, swimming, irrigation, food processing, washing, water system, and latrine flushing where possible; result obtained address probability appropriations as opposed to guiding evaluations toward diminishing vulnerability (Gitter et al., 2020; Odiyo et al., 2020; Kundu et al., 2018). It gives an outline proportion of people's wellbeing, permitting a correlation of impacts across a wide range of human health (Chen et al., 2021). A low contamination range,  $>0$ , is determined as good health but higher  $<1$  is considered poor health. The QMRA employs quantitative methodology through simulation strategies and displaying; this follows a fourstage process - dose-response, identification of hazard, risk characterization, and assessment exposure (Soller et al., 2016), Studies that recorded QMRA results using these stages have been conducted by Irda Sari et al., (2018); Odiyo et al., (2020); Ahmed et al., (2020).

### **2.9.1 Hazard Identification**

Hazard Identification involves identifying the pathogens and the nature of their adverse health effects on humans. *E. coli* O157:H7, was one of the pathogens selected for risk assessment since its occurrence is associated with human ill-health like diarrhoea. This is supported by reported studies of Daniels et al., (2016); Menon et al., (2016); Platts-Mills et al., (2015) and Robertson et al., (2015). This pathogen has worldwide recognition and is known to be transmitted via food and the environment (Haas et al., 1999). Studies by Owen et al., (2020); Odiyo et al., 2020) multiplied the dose of *E. coli* by 0.08 and the results indicated that only

8% of *E. coli* are pathogenic. A previous study by Ahmed et al., (2020) used pathogen ratios which were established by other researchers to determine *E. coli* pathogen risk with a ratio of *E. coli* 1:08.

### 2.9.2 Dose-Response Assessment

The assessment of dose-response (D-R) involves showing the relationship between the pathogen's dose and occurrence of an adverse consequence based on the contamination and illnesses using Beta-Poisson model Equation (2.1). Other models such as  $\beta$  -Poisson D-R, exponential D-R, and  $\beta$  -binomial D-R models have been used by other researchers for risk assessment (Kundu et al., 2018).

$$P_{inf/day} = 1 - \frac{(1 + \frac{d}{N_{50}})}{(2^{1/\alpha} - 1)^{-\alpha}} \dots \dots \dots \text{Eq 2.1}$$

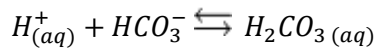
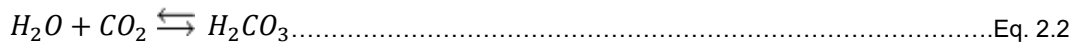
Where: d= dose;  $N_{50}$  is the dose corresponding to the median response, and  $\alpha$  is the alpha;  $P_{inf/day}$  = probability of infection for one exposure per day. The study by Ahmed et al., (2020) also used the  $\beta$  -Poisson (Eq. 2.1) D-R model to determine the potential risks that are associated with *E. coli*. Other studies have shown that the D-R model is considered the easiest model that estimates pathogens distribution between the random doses and follows Poisson distribution (Kundu et al., 2018; Odiyo et al., 2020).

#### Exposure through uses of water sources

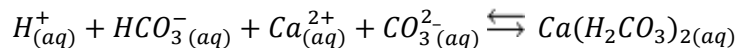
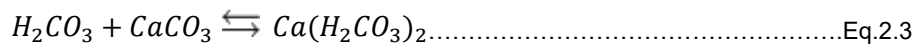
A study established that the number of days per year estimated when spring water was used from a source is a total of 203 days; whereas the rest of the days communities were using their boreholes/taps, were on vacations, or those days were public holidays (Odiyo et al., 2020; Ahmed et al., 2020). Through previous studies, it was estimated that a person consumed 1 litre of water per day (Machdar et al., 2018; Howard et al., 2016).

### 2.10 Geochemistry controlling spring waters

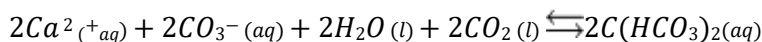
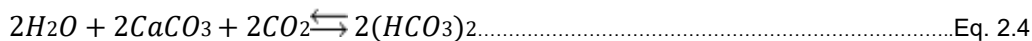
Various chemical reactions are generally between the water and rocks in the deep aquifer (Elango and Kannan 2007; Li et al., 2015). Some reactions occur within the water, and these regularly include anions or potentially metal cations/minor components (Hodder, 2005). As the water enters the area of recharge, it initially goes down through soil, leaves, and debris on the shallow level. The organisms in the soil and garbage emanate carbon dioxide which is broken down in the water and weak carbonic acid is formed (Eq. 2.2).



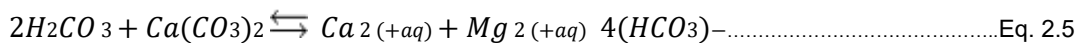
The acidic water in the earth further flows down through the different cherts of layers, this includes lathers which are thick (novaculite). The cherts and novaculite consolidate the spicules and skeletons of graptolites and radiolarians made of calcium. This calcium, close by the stone, exists in calcium carbonate  $CaCO_3$ . As the water flow through the formation of the cherts, it breaks up into pieces of the calcium carbonate (Olivier et al., 2010). The carbonic acids that are in the groundwater react with the calcium carbonate to form dissolvable calcium bicarbonate (Eq 2.3).



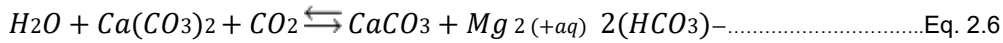
In this interaction, there is partially neutralized carbonic, which progressively become more alkaline. The solution, however, exists as calcium bicarbonate and will move onto the earth and break from the layers of the rock into silica (Hodder, 2005; Durowoju et al., 2019). When the  $C(HCO_3)_2$  solution reaches the surface, dissolved ( $CO_2$ ) carbon dioxide rapidly get to be released as displayed in Eq. 2.4:



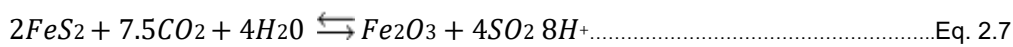
The chemistry of groundwater is mainly controlled by dissolution of  $Mg^{2+}$  and  $Ca^{2+}$  containing minerals (carbonate dissolution) (Akram et al., 2011) as shown in equations 2.5 below. This reaction may be written for dolomite dissolution.



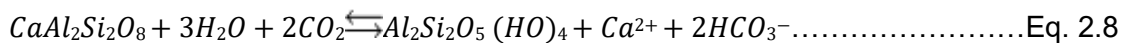
The calcite reaction dominates the early dissemination, creating a calcium bicarbonate water of shallow flow. When calcite saturation is reached, the prevailing reaction turns into an incongruent reaction of dolomite dissolution, as shown in Eq. 2.6 (Kimball, 1980; White, 2010).



The sulfate variety is like that of sodium and proposes a continuous increase beyond because of evaporative concentration. The reaction contributing to sulfate in the groundwater is shown in Equation (2.7). The reaction is mostly responsible for decreasing pH, which would expand an attack on carbonate and feldspar minerals. The absence of evaporite beds in the recharge regions blocks the contribution of sulfate from the disintegration of gypsum, although some of it can be found in surface breaks in the groundwater which had evaporated during the dry periods. This may be broken up and added to sulfate in the solution (Kimball, 1980; Daniele et al., 2013).



The silicate rock hydrolysis tends to be key in geochemical process, which determines the critical particle of the groundwater chemistry and results of  $Na^+$ ,  $Mg^{2+}$ ,  $K^+$  and  $Ca^{2+}$  and  $HCO_3^-$  being present in the groundwater (Appelo and Postma 2005; Clark 2015). Minerals of silicate are the principle parts of the volcanic stone springs in the region. The silicate hydrolysis is also constrained by the take-up of  $CO_2$  in the review region (Darling et al., 1996). Bicarbonate content are linked with dissolved cations (Haji et al., 2021) as shown in Eq 2.8 in the accompanying responses given below:



## 2.11 Water Types

The geochemical advancement of groundwater can be well understood by the Durov plot (Durov, 1948) and Piper's diagram (Piper, 1944). In the current review, a product called 'Geochemists Workbench Version 11.0.7 (GWB 11)' was utilized to plot these charts. The study conducted by Durowoju et al., (2019) had also reported conclusive results using this software. The Piper diagram is used to plot percentages of milliequivalents concentrations in relation with major cations ( $Na^+$ ,  $Mg^{2+}$ ,  $K^+$  and  $Ca^{2+}$ ); anions ( $Cl^-$ ,  $HCO_3^-$  and  $SO_4^{2-}$ ) are plotted in two three-sided fields, then projected further into the diamond field. Interestingly, the Durov graph is a composite plot comprising of 2 ternary charts where the milliequivalents rates of the cations of premium were plotted against anions, sides structured as focal rectangular and parallel plot of complete cation versus all concentration of anion are performed (Durov, 1948). Both graphs can uncover and contrast spring water since those with comparative characteristics will quite often plot together as groups (Saha et al., 2019). Piper's diagram, however, provides information plotted on the subdivisions of formed triangle

diamond fields which evaluate the water type in a spring water. Conversely, convergence of lines, stretched out from the places in ternary outlines and projected on the sub-divisions of double plot of Durov plot characterize the process of hydrochemical required, alongside water type. The current research has used Durovs and Pipers diagrams to assess the water types of groundwater/spring water (Jalees et al., 2021; Hosseinifard et al., 2015; Durowoju et al., 2019; Musaed et al., 2020).

## 2.12 Methods for monitoring spring water quality

Table 2.3: Shows Analytical methods for water quality

ICP-MS	ICP-OES	AAS	Membrane Filtration	The multiple-tube method
ICP-MS advantage is that offers results below detection level	Utilized for every one of the grids of ecological/environmental samples, particularly, for high-framework tests	Simple and quick to utilize. It is used to evaporate the solvent and separate the example into its particles.	It is based on the entrapment of bacterial cells by sterile membrane filter with 0.4 um pore sizes	Referred to as the Most Probable Number (MPN) method because it is based on an indirect assessment of microbial density in the water
Wide dynamic range	Generally is a less expensive choice if the element does not need a detection limit that is lower than what the ICPMS conveys	Relatively few interferences	Quicker: quantitative outcomes (18 hours)	It is time-consuming to perform and requires more equipment, glassware, and consumables. It is slower: requires 48 hours for a positive M
Productively eliminates polyatomic obstructions utilizing impact cell innovation	Less difficult strategy which does not need an expert with specialized aptitude	Very compact instrument	Less labourintensive	More labourintensive.
Rapid semiquantitative analysis	It is sufficient for grade analytical reagents only	Good performance	Not application to high turbid water	It is essential for highly turbid samples
Isotopic analysis	Spectral interferences possible	Robust interface	Requires less culture medium	Applicable to all types of water

Specialisation capacity	High total dissolved solids and productivity	1-10 elements per determination	The precision is high. Colonies are counted to directly get the results.	It is determined as low precision. Approximation statistical analysis is utilized to obtain results
Methods:  EPA 321.8 (IC-ICP-MS)  ISO 17294-2:2016 NEN 6427:1999	Regulatory methods  EPA 6010  ISO 11885:2007 N0252  NEN 6426:1995	Moderate detection limits and element limitations	Consumables' cost is high in many countries.	Consumables very accessible in many nations and gives better recuperation.

Source: Ninfa *et al.* (2019); Edokpayi *et al.* (2015); Hossain *et al.* (2021); Suresh *et al.* (2019); Njoyim (2016)

## CHAPTER THREE

### METHODOLOGY

#### 3.1 Research design

This research aims to evaluate water quality, potential uses, and health risks associated with spring water in Thulamela Municipality (TM). This was a quantitative study in which water samples were collected from various springs at TM and analyzed at the laboratories for physical, chemical, and microbiological parameters. Information was gathered in a standard manner and estimated numerically for proper statistical investigation. Relationship of the analysis was carried out, in which a control was utilized to guarantee the validity of information obtained.

#### 3.2 Methods and Materials

##### 3.2.1 Collection and sampling of spring water

Three sets of 41 water samples were collected (for microbial, metals and non-metals analysis) from different springs (Appendix 3) at Thulamela Municipality (Tshifulanani, Ngovhela, Tshakhuma, Mavhunda, Dzindi, Tshifulanani, Golgotha, Ngovhela, Mapate, Niani, Mandala, Milaboni, Dipeni, Tshikunda, Lwamondo, Mukondeni, Makhuvha, Makwarela, Maungani, and Mapate) (Table 3.1; Appendix 7). These representative samples were obtained by random selection, and the water from all aspects of the spring, was taken with a sterile plastic cup (Fisher et al., 2015). The samples were collected monthly from (August-October 2020) for dry and (November-January 2020/2021), wet season. The spring water was collected into plastic containers and sterile sampling bags from the springs before transporting them for pretreatment (Yuan et al., 2022). Each sampling container was labelled immediately after collection, maintained at 4°C, and transported to the laboratory of the Department of Hydrology and Water Resources (Univen) for further analysis. One set of the samples was acidified with 3 ml of nitric acid for trace elements investigation (Machona et al., 2017; Durowoju et al., 2016).

**Table 3.1: Sampling points and geological locations**

Samples ID	Spring's Name	Coordinate (s)		Elevation (m)	Direction
		Latitude	Longitude		
S1	Thohoyandou Golgota	22° 58.028' S	30° 25.927' E	581	E
S2	Maugani Khopha	22° 56.674' S	30° 22.752' E	710	NW
S3	Maungani 1 Magoro	22° 58.156' S	30° 25.185' E	613	NW
S4	Maungani 2 Mugigigi	22° 58.155' S	30° 25.187' E	615	NW
S5	Maungani 3 Sasol	22° 59.290' S	30° 25.309' E	582	SW
S6	Duthuni bridge Tshitlokwe	22° 58.035' S	30° 25.599' E	630	West
S7	Duthuni bridge Tshiungulwi	22° 58.029' S	30° 25.595' E	633	West
S8	Duthuni musada Tshiseluselu	22° 59.093' S	30° 23.665' E	605	West
S9	Duthuni musada Iwandani	22° 59.090' S	30° 23.665' E	604	West
S10	Lwamondo Nemutandani	23° 00.813' S	30° 21.900' E	639	SW
S11	Tshifulanani Zwininani Up	23° 02.647' S	30° 23.282' E	595	SW
S12	Tshifulanani Madzhatshise	23° 02.817' S	30° 23.540' E	613	SW
S13	Tshakhuma Luhuyuni	23° 03.699' S	30° 19.697' E	644	SW
S14	Tshakhuma Thavhani A	23° 03.413' S	30° 19.413' E	686	SW
S15	Tshakhuma Thavhani B	23° 03.411' S	30° 19.641' E	687	SW
S16	Tshakhuma Tshiomvani A	23° 04.017' S	30° 19.068' E	618	SW
S17	Tshakhuma Tshiomvani B	23° 04.016' S	30° 19.066' E	615	SW
S18	Tshakhuma ZCC	23° 03.658' S	30° 17.554' E	638	SW
S19	Tshakhuma Mulangaphuma	23° 03.333' S	30° 17.744' E	655	SW
S20	Dzindi	22° 52.385' S	30° 30.803' E	580	NE
S21	Manini ZCC Tshidududu	22° 59.199' S	30° 29.368' E	559	E
S22	Ha Mavhunda 1	22° 56.647' S	30° 30.502' E	554	NE
S23	Ha Mavhunda 2	22° 56.422' S	30° 30.599' E	620	NE
S24	Makwarela	22° 57.258' S	30° 29.120' E	722	E
S25	Makhuvha Zwidengani	22° 58.381' S	30° 25.299' E	679	West
S26	Makhuvha 1	22° 52.321' S	30° 30.853' E	611	NE
S27	Makhuvha 2 Lutande	22° 52.319' S	30° 30.851' E	617	NE
S28	Ngovhela 1 (up)	22° 57.493' S	30° 25.550' E	693	N
S29	Ngovhela 2	22° 57.501' S	30° 25.548' E	721	N
S30	Phiphidi 1 Tshimpfulusuli	22° 56.922' S	30° 22.534' E	785	NW



S31	Phiphidi 2 Gambudzi	22° 56.637' S	30° 22.579' E	790	NW
S32	Phiphidi 3 Thovholo	22° 56.647' S	30° 22.572' E	797	NW
S33	Phiphidi 4 Phathuli	23° 03.699' S	30° 18.276' E	690	SW
S34	Tshivhilidulu 1	22° 55.287' S	30° 13.778' E	810	West
S35	Tshivhilidulu 2 Muhuyuni	22° 55.219' S	30° 13.485' E	817	West
S36	Tsgivhilidulu 3 Muhuyuni	22° 55.250' S	30° 13.671' E	814	West
S37	Mandala	22° 55.119' S	30° 13.151' E	794	West
S38	Shanzha Dandani	22° 55.123' S	30° 13.150' E	811	West
S39	Milaboni Lirini	22° 53.438' S	30° 14.094' E	918	NW
S40	Tshikombani 1	22° 53.517' S	30° 14.306' E	953	NW
S41	Tshikombani 2	22° 53.520' S	30° 14.309' E	948	NW

### 3.3 Experimental Procedures: Spring water analysis

#### 3.3.1 Determination of some Physicochemical Parameters

A measurement of some physicochemical parameters was carried out *in situ* and in the laboratory. On-site measurements parameters included temperature, pH, EC, salinity, and total dissolved solids (TDS) using Extech Multimeter measurements (Combo HI 98130, USA). Turbidity meter was utilized to determine the water turbidity after calibration of the instrument following the manufacturer's guidelines (Varol and Davraz, 2015). The results of the spring water samples were then compared with the standard guidelines of DWAF/SANS and WHO for drinking water, agriculture, irrigation, and recreation to establish if the spring water is safe for human consumption (Varol and Davraz, 2015). Furthermore, for accuracy, spring water samples were measured in triplicate.

#### 3.3.2 Major metals analysis

Thermo ICap 6200, Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Chemetix Pty Ltd., Johannesburg, South Africa) was used to analyse major metals ( $Na^+$ ,  $Mg^{2+}$ ,  $P$ ,  $K^+$  and  $Ca^{2+}$ ) of various spring water samples. The National Institute of Standards and Technology traceable guidelines (NIST, Gaithersburg, MD, USA) bought from Inorganic Ventures (Inorganic ventures 300 Technology Drive Christiansburg, Christiansburg, VA, USA) were utilized for adjustment of the instrument for the evaluation of chosen major metals. A NIST-recognizable quality control standard from De Bruyn Spectroscopic Solutions, Bryanston, South Africa, were analysed to check the accuracy of the adjustment before analysing the samples (Edokpayi et al., 2018; Batool et al., 2018).

### **3.3.3 Trace elements Analysis**

The trace elements in water source were analysed using an Agilent 7900 Quadrupole inductively coupled plasma mass spectrometer (ICP-MS) (Chemetix Pty Ltd., Johannesburg, South Africa). The samples of spring water were presented by means of a 0.4 mL/min ( $7 \times 10^{-9} \text{ m}^3 \text{ s}^{-1}$ ) micro-mist nebulizer into a Peltier-cooled splash chamber with a temperature of 2°C (275.15 K), using the transporter gas stream 1.05 L/min ( $1.75 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$ ). The components B, Al, V, Mn, Fe, Co, Ni, Cu, Zn, Cr, As, Se, Sr, Mo, Cd, Sn, Sb, Ba, Hg, Pb and Si were examined under He-crash mode to eliminate polyatomic obstructions. NISTdetectable guidelines were utilized to adjust the equipment.

### **3.3.4 Major Anions analysis**

The major anions analysis which included  $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $NO_2^-$ , Br,  $PO_4^{3-}$  and  $SO_4^{2-}$  in spring water was analysed using Ion Chromatography (IC). An eluent was prepared using the suitable chemicals and reagents ( $Na_2CO_3$ ,  $NaHCO_3$ ,  $HPO_3$  standards). Ultrapure water was used to prepare the calibration standards (Merck-Millipore, Molsheim, France).

Anion analysis was performed on a Metrohm 930 Compact IC Flex broiler/SES/PP/DEG (Metrohm, Herisau, Switzerland) furnished with a segment stove, MSM and MSC module for successive concealment, peristaltic siphon for silencer recovery and an implicit degasser. An auto sampler (858 IC Professional Sample presser, Herisau, Switzerland) was coupled with the chromatograph for sample introduction. A Metrosep A Supp 5 column separation (4.0 x 100 mm) linked with Metrosep A Supp 5 column guard was used for separation of the ions.

### **3.3.5 Geospatial Distribution Analysis**

An investigation with respect to spatial distribution of spring water data was done by the spatial arrangements of data using geo-statistical modelling of Thulamela Municipality. GIS software (ArcGIS Geostatistical Analyst 10.8) was utilised in this study and location points were traced with GPS to generate spatial distribution maps of the concentration in spring water samples of the study area (Xu and Zhang, 2022).

### **3.3.6 Estimation of bicarbonate**

Bicarbonate ( $HCO_3^-$ ) values were determined using the equation of Granat (1972) based on pH values measured:

$$HCO_3^- = 10^{-11.25+pH} \text{ in (Meq/L)}$$

After computation of bicarbonate results for ion balance observation, the relation between pH and  $HCO_3^-$  concentrations presence in water was also determined (Anatolaki and Tsitouridou, 2009) (Figure 3.1 below). The chemical conversion factor of  $O_3^-$  from millimole/litre to milligram/Litre SI units was multiplied by 61.02 (Anatolaki and Tsitouridou, 2009).

The analysis of correlation application was computed using excel; the results between pH and  $HCO_3^-$  concentrations gave a linear equation of  $y = 8.5816x - 55.537$  (dry) and  $y = 37.712x - 272.71$  (wet) to indicate important role and presence of  $HCO_3^-$  in spring water of Thulamela Municipality.

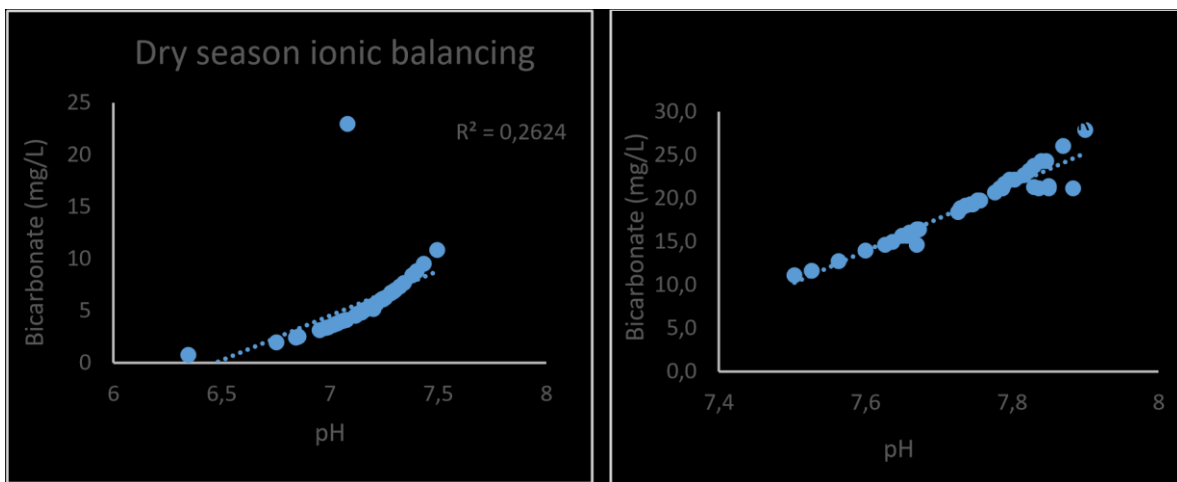


Figure 3.1: Showing dry and wet season data fits to estimate bicarbonate

Linear equations computed were used to estimate  $HCO_3^-$  accurate concentrations, using Component of Correction Factor (CCF) on excel. Through this, pH was plotted on the x axis while bicarbonate was plotted on the y-axis. The bicarbonates measurements for both seasons, linear regression analysis between the measured and calculated, showed significant correlation. Figure 3.2 below shows the linear graphs drawn of the wet and the dry seasons, using ionic balancing equations to estimate acute straight line y values of bicarbonate.

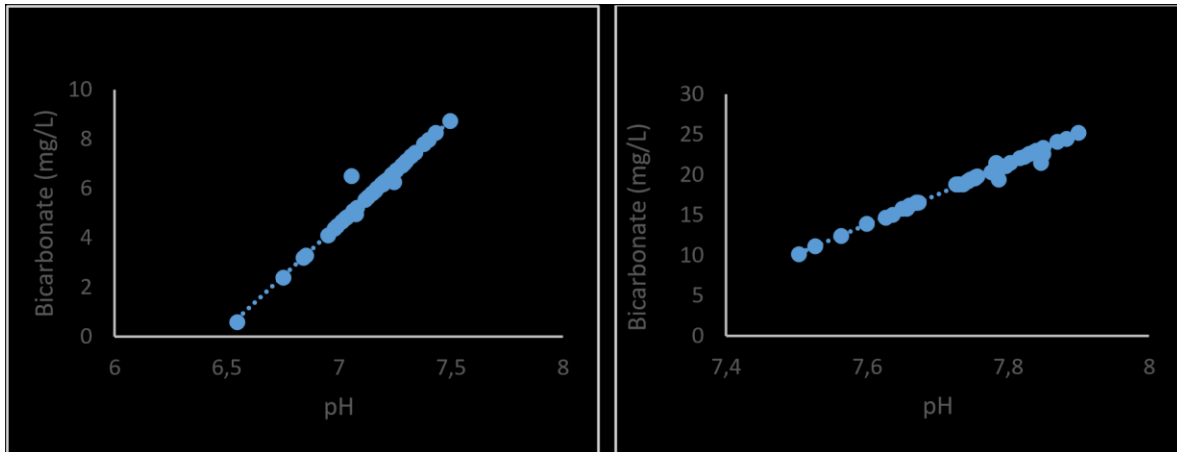


Figure 3.2: Estimating Bicarbonate values using Component Correction Factor

For more understanding of the evolution of geochemical spring water at Thulamela Municipality, the samples were plotted in Piper's (Piper, 1944) and Durov diagrams (Durov, 1948) using a software called 'Geochemists Workbench Version 11.0.7 (GWB 11)'. The Piper diagram was plotted in concentration of milliequivalents percentage of major cations ( $Na^+$ ,  $Mg^{2+}$ ,  $K^+$  and  $Ca^{2+}$ ) and anions ( $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $Br^-$ ,  $PO_4^{3-}$  and  $SO_4^{2-}$ ) were plotted in two triangular fields and further projected to a field of central diamond (Ravikumar et al., 2015). Durov's plot in this study was utilised to validate the processes' formations and validate types of water.

### 3.3.6 Microbiological preparations and determination

#### i. Preparation of M-Tec ChromoSelect Agar (m-TEC Agar)

The preparation of the agar was done by adhering to the manufacturers (Sigma-Aldrich) instruction; 45.6 g of the agar was poured into 1 L of distilled water and boiled until it dissolved (EMD Millipore, Billerica, MA, USA). The medium was then sterilized at 121°C for 15 minutes using autoclave. The medium was cooled and poured into dishes that were sterile, thereafter, it incubated for 24 hours at 44°C.

#### ii. Preparation of M- Endo Agar Les

Preparation of the medium was done using the instructions from the manufacturer (Biolab) (HG000C74.500); 51 grams of powder was suspended in 1 L of distilled water. After which, 20 ml of ethanol was added and the medium was left to stabilize for 10 minutes. Subsequently, it was boiled until it completely dissolved. It was then cooled before being pouring into petri dishes that were sterile.

### iii. Preparation of *m*-FC Agar Les

Preparation of the medium was done using the calibration guideline from the manufacturer (Biolab) (HG000C92.500) (Biolab, Merck, South Africa). 50 grams of agar was suspended in 1 L distilled water. 10 mL of 1% rosolic acid was added in 0.2 N NaOH to the medium and was left to stabilize after stirring for 10 minutes. After stabilizing, it was boiled until it completely dissolved. It was then allowed to cool before being poured into sterile petri dishes.

### 3.3.7 Determination of bacteriological parameters

The spring water samples were analysed within the 6 hours recommended by the (Younus, 2021). A 100 mL of test solution was filtered through a filter funnel containing a sterile 0.45  $\mu\text{m}$  cellulose filter paper and incubated for 24 hours at temperature suitable for the test organisms (Daghara et al., 2019). Some samples were diluted in the ratio of 1:10 and was filtered following same procedures. Some of the picture taken during lab work analysis were shown below (Figure 3.3).



Figure 3.3: Some pictures showing various components of the work done in the laboratory

### 3.4 Water quality Index (WQI)

Water Quality Index (WQI) is determined as an exceptional and critical rating method that computes the general water quality and presents the data in a more useful format to water managers (USEPA, 1989).

The standard indicated for drinking water (WHO, 2011 and SANS, 2015) was utilised for the estimation of WQI, via three phases. Initially, the physiochemical parameters were allocated

a weight ( $w_i$ ) due to their significance in drinking water (Equation 3.1). Parameters that are more significant to the assessment of water quality were assigned maximum weight of 5, and the ones considered not significant were given a weight of 1. The weight ( $W_i$ ) values of each parameter were measured using (Equation 3.1)

$$WI = \frac{w_i}{\sum_{i=1}^n w_i} \dots\dots\dots 3.1$$

$WI$  -is the unit weight of pollutant variable;  $n$ - is the number of pollutant variable;  $w_i$ - is the weight of each parameter.

The scale of quality rating ( $q_i$ ) for each parameter (Equation 3.2) was found by dividing it's concentration in the spring water values, by the desired threshold guidelines, and the result was multiplied by 100.

$$q_i = (C_i/S_i) * 100 \dots\dots\dots 3.2$$

$q_i$ - rating quality,  $C_i$  - concentration of spring water in (mg/L), and  $S_i$  - standard limit of drinking water for studied chemical elements in (mg/L).

For computing WQI,  $q_i$  and  $W_i$  were used as shown in Eq. (3.3) below (Brown *et al.*, 1972; Li *et al.*, 2010; RamyaPriya and Elango, 2018). Table 3.2 below shows the rating of water quality status.

$$WQI = \sum_{i=1}^n WI * q_i \dots\dots\dots 3.3$$

Table 3.2 shows the rating based on WQI

<i>WQI</i>	<i>Water Quality status</i>	<i>Grading</i>
51	Excellent	A
51-100	Good	B
101-200	Poor	C
201-300	Very poor	D
>300	Not suitable for drinking purposes	E

Source: Asare-Donkor et al., 2016

### 3.5 Health risk assessment associated with Trace Metals in spring water

The dose exposure to determine human health risks through two pathways (dermal and ingestion) were described and can be determined by the use of Eqs. 3.4 and 3.5 as adjusted from the US EPA hazard appraisal guidance (USEPA, 1989; Asare-Donkor et al., 2016).

$$Exp_{ingestion} = \frac{C_{water} \times IR \times EF \times ED}{BW \times AT} \dots\dots\dots 3.4$$

$$Exp_{derm} = \frac{C_{water} \times SA \times KP \times EF \times ET \times ED \times CF}{BW \times AT} \dots\dots\dots 3.5$$

$C_{water}$ : estimated trace elements in spring water ( $\mu\text{g/L}$ ),  $Exp_{ingestion}$ : dose through ingestion exposure of water ( $\text{mg/kg/day}$ );  $Exp_{derm}$ : dermal exposure dose ( $\text{mg/kg/day}$ );  $R$ : ingestion rate in this study;  $EF$ : exposure frequency  $ED$ : exposure duration  $BW$ : body weight average;  $SA$ : exposed skin area ( $\text{cm}^2$ );  $KP$  ( $Cd, Fe, Mn, Ba, Cu$  (0.001); (0.002);  $Pb$  (0.04);  $Ni$ ; (0.002);  $Zn$  (0.0006) : dermal permeability coefficient in water;  $ET$ : exposure and  $CF$  :unit conversion factor as shown in (Table 3.3) below.

Table: 3.3 Health risk assessment of different exposure through parameter

Parameter	Unit	Child	Adult
Exposure Frequency (EF)	Day/year	365	365
Body Weight (BW)	Kg	15	70
Exposure Duration (ED)	Years	6	70
Skin surface Area (SA)	$\text{cm}^2$	6600	18000
Ingestion Rate (IR) or Daily intake (DI)	L/day	1.8	2.2
Exposure Time (ET)	Hours/day	1	0.58
Conversion Factor (CF)	$\text{L}/\text{cm}^3$	0.001	0.001
Averaging Time (AT)	Days	$365 \times 6$	$365 \times 70$
Particular Emission Factor (PEM)	$\text{m}^3/\text{kg}$	$1.3 \times 10^9$	$1.3 \times 10^3$

Source: (USEPA, 1989)

Possible non-cancer risks due to exposure of trace elements selected were computed by dividing the determined toxin pathways (ingestion and dermal) with the reference dose (RfD) ( $\text{mg/kg/day}$ ) (USEPA, 1989) utilizing Eq. 3.6 to determine hazard quotation (HQ) capability of everyday intake according to reference dose, for an individual, through the two pathways.

$$HQ_{ing/derm} = \frac{Exp_{ing/derm}}{RfD_{ing/derm}} \dots\dots\dots 3.6$$

$HQ_{ing/derm}$  is ingestion/dermal poisonousness dose reference (mg/kg/day). To survey the general potential non-cancer-causing impacts presented by more than one metal and pathway, the amount of the registered HQs across trace elements was communicated as Hazard Index (HI) utilizing Eq. 3.7 (USEPA, 1989), (Table 3.4).

$$HI = \sum_{i=1}^n HQ_{ing/derm} \dots\dots\dots 3.7$$

$HI_{ing/derm}$  is hazard index via ingestion

Table 3.4: shows  $RfD_{ing}$ ;  $RfD_{derm}$ ;  $SF_{ing}$  through exposure was determined using Eq. 3.8

Parameters	$RfD_{ing}$	$RfD_{derm}$	$SF_{ing}$
Mn	2.40E-02	1.43E-03	N/A
Fe	7.00E-01	1.40E-01	N/A
Ni	2.00E-01	5.40E-03	910
Cu	3.70E-02	2.40E-02	N/A
Zn	3.00E+00	7.50E-02	N/A
Cr	3.00E-03	3.00E-03	500
As	3.00E-04	3.00E-04	N/A
Mo	5.00E+00	2.50E-02	6100
Cd	1.00E-03	1.00E-03	N/A
Ba	2.04E-04	2.00E-02	8.5
Pb	3.50E-03	5.25E-04	N/A

Source: USEPA (1989)

$$CR_{ingestion} = Exp_{ingestion} / SF_{ing} \dots\dots\dots 3.8$$

$SF_{ing}$ - slope factor for carcinogenic computation

$CR_{ing}$ - carcinogenic risk via ingestion exposure

### 3.6 Risk Characterization or Quantitative Microbial Risk Assessment (QMRA)



The risk characterization included each of the various steps (characterization of hazard, response of dose evaluation and exposure assessment) to determine the contamination probability and disease per year. In the dose-response computation and evaluation, the *E. coli* concentration found was duplicate by 0.08 (8%) of *E. coli* pathogenic (Owens et al., 2020; Odiyo et al., 2020); this was used to determine the risk from microbial microorganisms from exposure to spring water.

The probability of annual infection was calculated using Equation (3.9): They were determined by the standard equation used by Kundu et al. (2018)

$$P_{inf/day} = 1 - (1 + \beta)^{-D - \alpha} \dots\dots\dots 3.9$$

$P_{inf/day}$  probability of daily infection (%),  $D$  - dose ingested average, and  $\alpha$  and  $\beta$  are parameters for the dose-response (Table 3.5).

Table 3.5: Dose-response assessment parameters

E.coli 0157-Outbreak data	Parameter used in estimation	References
Adult	$\alpha = 0.050$ ; $\beta = 1.001$ ; $P_{iil/inf} = 0.35$	Shinagawa et al. (1997); Teunis et al., (2004); Haas et al., (1999)
Child	$\alpha = 0.084$ ; $\beta = 1.44$ ; $P_{iil/inf} = 0.35$	

Equation (3.10) below was used to compute risk of infection per year (%)

$$P_{infannual} = 1 - (1 - P_{inf/day})^n \dots\dots\dots 3.10$$

Where the probability infection per day  $P_{inf/day}$  was obtained above, and  $n$  is the number of exposure days in a year,  $n=203$

**Probability of illness per year:**

The estimation of illness probability per year/annual was used to determine the number of cases of diseases per year, per person, Equation (3.11) was used.

$$P_{iil} = P_{infannual} \times P_{iil/inf} \dots\dots\dots 3.11$$

Where,  $P_{iil}$  is the risk of annual illness

### **3.7 Statistical analyses**

Average values of physiochemical and microbial analyses were presented. Information obtained from the study was exposed to factor investigation. Data acquired from this study were displayed in tables and graphs using excel spread sheet (Durowoju *et al.*, 2016). Data, thereafter, was subjected for statistic measurements to determine the standard deviation, correlation and in all cases,  $p < 0.05$  is the accepted significance level (Durowoju *et al.*, 2016).

## CHAPTER 4 RESULTS AND DISCUSSION

### Introduction

The chapter is a presentation of the results from the field and laboratory analyses conducted, as well as the implications of the data obtained. The data in this chapter are analysed and represented in graphs, maps and table forms. The collected spring water samples' results were analysed in both dry and wet seasons.

### 4.1 Physical parameters

#### 4.1.1 Electrical Conductivity (EC)

EC is a measure of electrical conductivity in any solution. EC detected was in a range of 45.9224.76 (dry) and 51.13-339.96 (wet) mS/m. The highest value of EC was found at S34 (339.96) and the lowest value at S40 (45.9) (Figure 4.1). The mean of EC in the wet season was  $121.29 \pm 52.67$  and  $149.38 \pm 67.83$  in the dry season. The average level of EC was high in the wet season compared to the dry season and the presence of EC concentration may be due to agricultural activities and runoffs that were observed. All sampled springs around Thulamela Municipality were within the standard guideline for drinking water of SANS  $\leq 1700$  mS/cm and WHO  $< 0-600$  mS/m (SANS, 2015; WHO, 2011); they also fell within the guidelines of WHO for irrigation purposes (3000 mg/L) (Appendix 1).

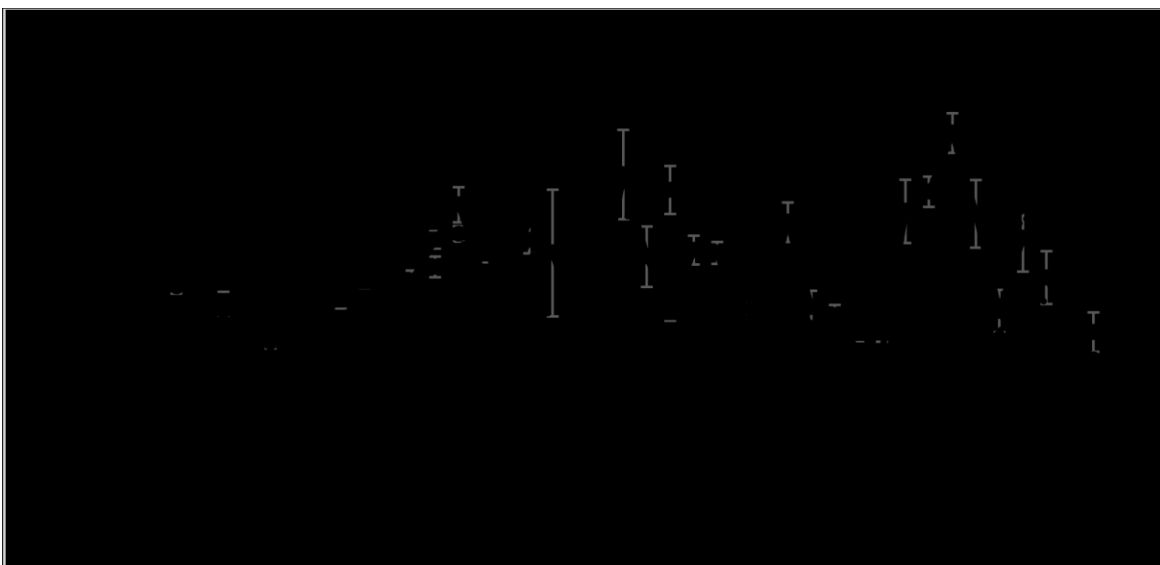


Figure 4 1: EC variation in water samples

The revealed EC difference in the average level of the spring water during the dry and wet seasons did not differ significantly ( $P > 0.05$ ). Pearson's correlation matrix was also computed in this study to assess the interrelationships among various spring water quality parameters of the study area (Thulamela Municipality) for the dry and wet periods (Appendix 5 and 6). The spatial distribution of EC at Thulamela Municipality is shown in Figure 4.2; the highest EC levels were determined in the north-eastern region.

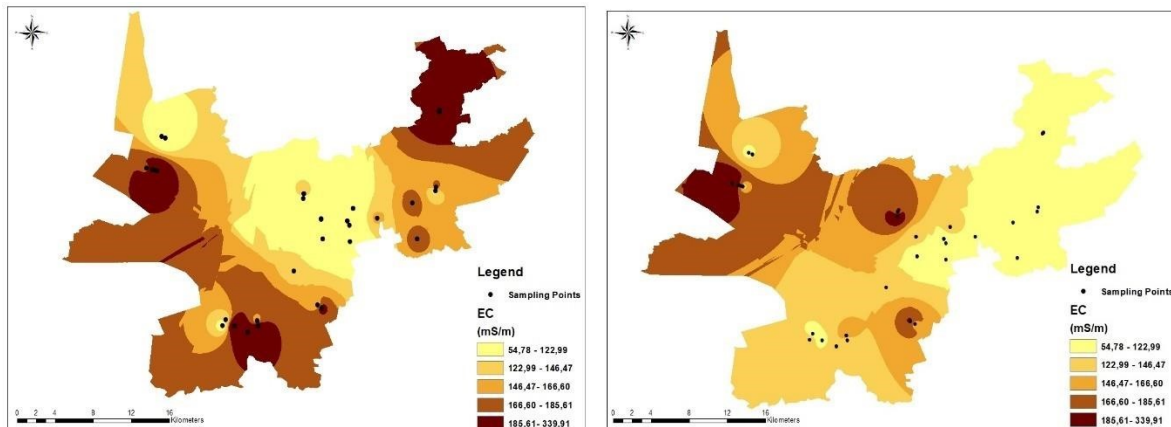


Figure 4.2: Spatial Distribution of EC (A- wet season and B- dry season)

#### 4.1.2 Temperature

Temperature is critical for the management of aquatic ecosystems and effective protection. It is essential to water bodies concerning the metabolic rates of living organisms and chemical reactions, and it serves as aquatic species controlling factor (Ologundudu et al., 2020). The average temperature recorded throughout the study ranged from 21.75 - 24.1°C (dry) and 22 – 25.23 °C for (wet) with a mean of  $22.5 \pm 0.795 \pm 0.588$  °C (dry) and 23.05 °C (wet) (Figure 4.3). The mean temperature measured in selected sampling areas of all the springs complied with the recommended guideline set by SANS and WHO - which is  $\leq 25$  °C (SANS, 2015; WHO, 2015). The results recorded were comparable to those obtained by Adejumo et al., (2018) which revealed a range of 24 to 25°C.

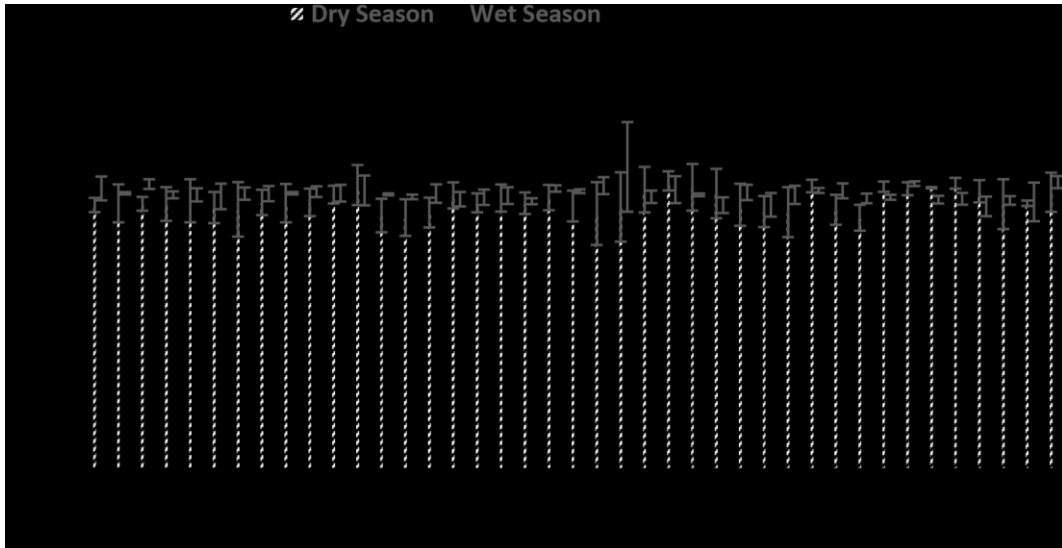


Figure 4.3 Mean temperature variation in water samples

The temperature levels of the dry and wet seasons were statistically different ( $P < 0.05$ ) with a p-value of 0.00071 (Appendix 2). The spatial-temporal distribution of temperature among the sampling sites is presented in Figure 4.4. It can be seen that seasonal variations have an impact on the temperature of the spring water. Another study that recorded high values of temperature was conducted by Durowoju et al. (2019) with a range between 41 - 49°C (hot) and 53 - 69 °C (scalding) within Soutpansberg, Limpopo Province, South Africa. Odiyo et al. (2020) reported that the temperature of the spring water samples varied from 22.1 to 27.6 °C in in Vhuronga 1, Limpopo Province, South Africa, and recorded comparable results to this study.

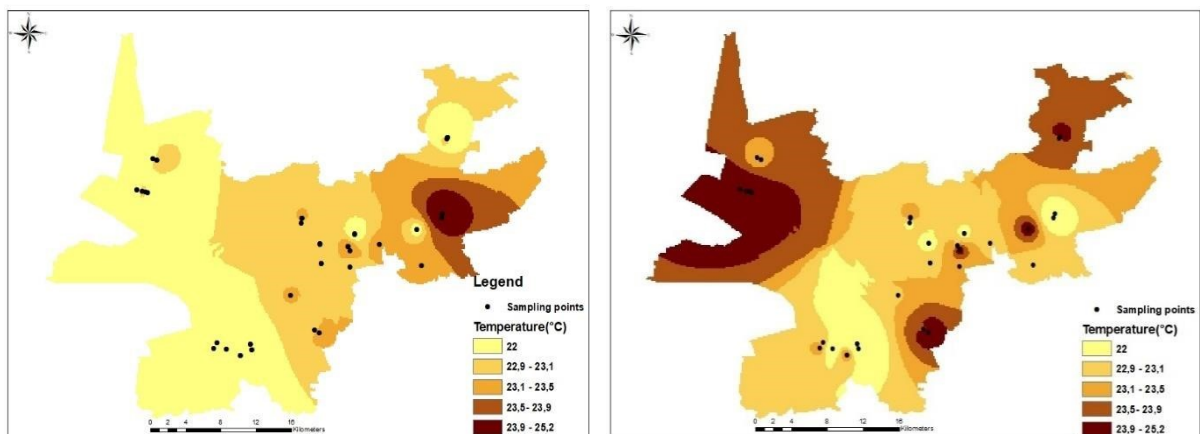


Figure 4.4: Spatial Distribution of Temperature (A- wet season and B- dry season)

### 4.1.3 pH

The measured pH in this study throughout the sampling period ranged from 6.67 - 7.4 (dry) and 7.5 – 7.88 (wet) with a mean of  $7.15 \pm 0.20$  (dry) and  $7.74 \pm 0.10$  (wet) (Figure 4.5). In all the observed spring water, the pH ranges were within the recommended guidelines of SANS (6.6 - 9.5) and WHO (6.5 - 8.5). The pH of 5.5 to 8.2 is generally considered to be the healthiest for diverse aquatic life (Edokapayi et al., 2018).

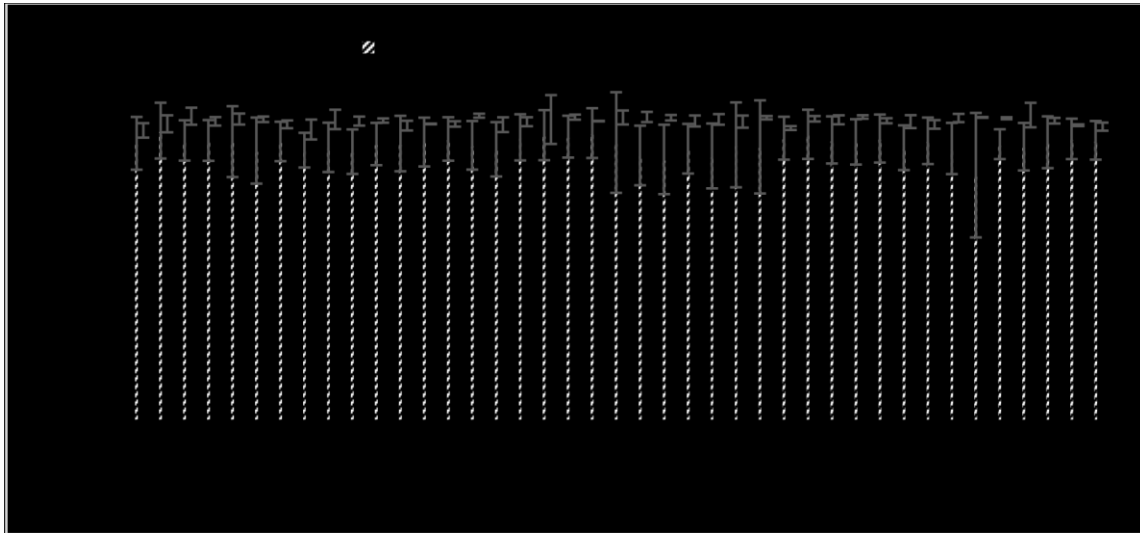


Figure 4.5: pH variation in water samples

Excessively high and low pH values can be detrimental for the quality of water. The results obtained were comparable to those obtained by Enitan-Folami et al., (2018) which were within a range of 6.04-7.17, hence, within the recommended limit. A comparable level of pH (7.7 to 9.3), however, was reported from different spring water by (Lalumbe et al., 2022) in Soutpansberg Region, Limpopo Province, South Africa. The geospatial levels of pH recorded in this study are presented in Figure 4.6.

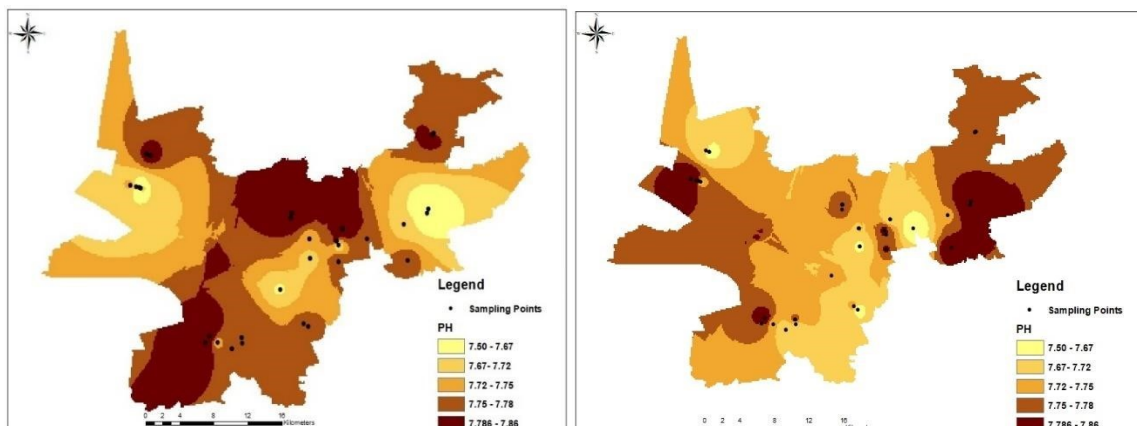


Figure 4.6: Spatial Distribution of pH (A- wet season and B- dry season)

#### 4.1.4 TDS

The revealed range of TDS varied from 35.7 -155.79 (dry) and 24.7- 236.03 mg/L (wet). The average values of TDS in the spring waters were  $101.13 \pm 69.26$  (wet) and  $100.2 \pm 47.79$  (dry) mg/L (Figure 4.7). All the springs' water were within the limit for drinking and domestic use of WHO (0-400 mg/L) and for livestock production (<1200 mg/L) (WHO, 2011; SANS, 2015). The TDS showed positive strong correlation with V, Na, Mg, Si, Ca, and F in the dry season and  $\text{NO}_3$  in the wet season (Appendix 5 and 6).

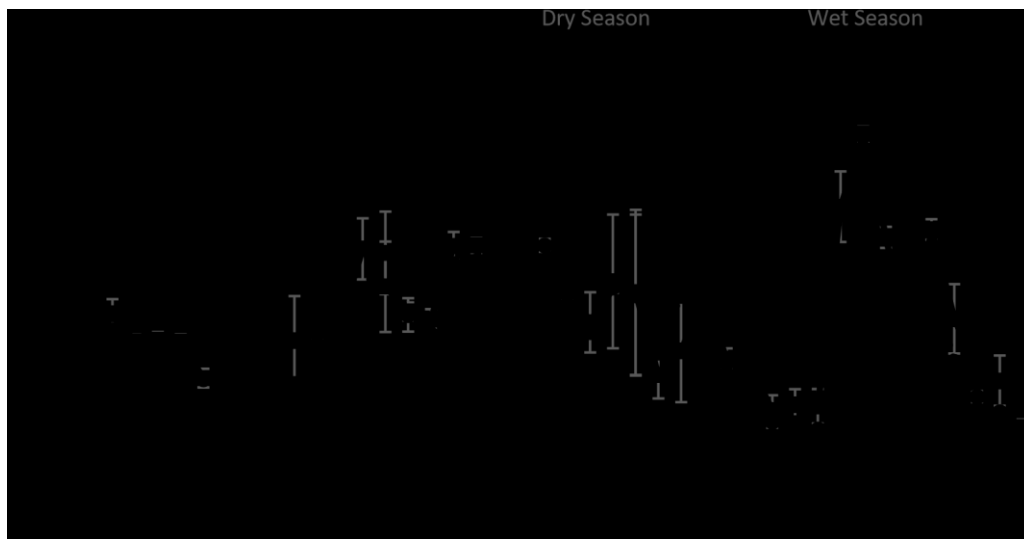


Figure 4.7: TDS recorded in water samples

The p values computed using the t-test revealed insignificant difference in the mean TDS level of the spring water for dry and wet seasons ( $P > 0.05$ ). Furthermore, the spatial distribution of TDS in the wet season was high in the south-west and north-east of the study area (Figure 4.8). The presence of TDS may be due to sewage, run-offs, and agriculture activities. As expected, there was a strong correlation between TDS and EC ( $r = 0.96$ ) (dry) and ( $r = 0.87$ ) (wet) because they are directly proportional to each other; when conductivity increases, the concentration of all dissolved constituents/ions increases. EC in the dry season showed a strong positive correlation with Mn, Co, Ni, Cr, Sn, Ba,  $\text{NO}_3$ , FC, and *E. coli*, whereas a strong correlation in the wet season was with salinity, TDS, and  $\text{NO}_3$ . The results obtained were lower compared to those reported by Lalumbe and Kanyerere (2022) which were within a range of 80 to 1869 mg/L.

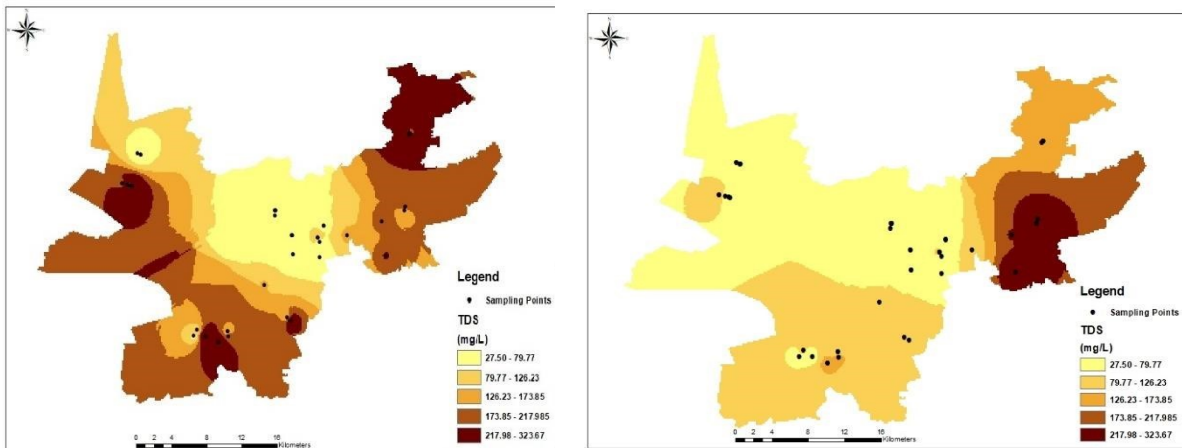


Figure 4.8: Spatial Distribution of TDS (A- wet season and B- dry season)

#### 4.1.5 Salinity

The salinity in all the springs studied were within the recommended guideline level by WHO (100-500 mg/L) and SANS (<1500 mg/L). Salinity concentration revealed in this study ranged from 22.5- 142.21 (dry) and 36- 217.43 mg/L (wet). The recorded average values were  $66.46 \pm 29.78$  (dry) and  $80.45 \pm 45.18$  mg/L (wet) (Figure 4.9).

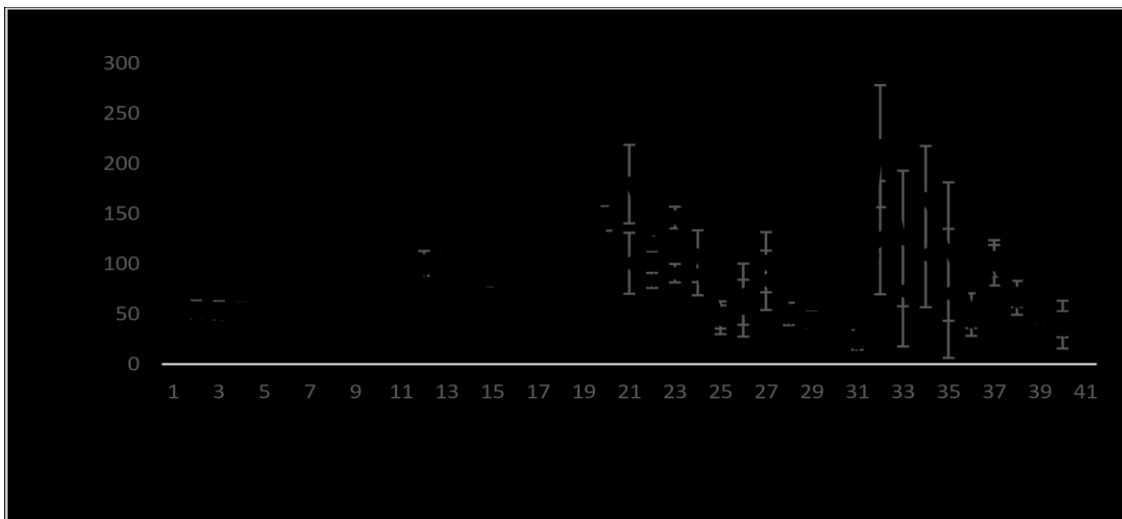


Table 4.9: Spatial Distribution of Salinity (A- wet season and B- dry season)

Salinity showed a positive correlation with TDS and some metals in the dry season and only TDS in the wet season (Appendix 6). There was a statistically insignificant difference in the obtained means of salinity in the studied seasons ( $p < 0.05$ ) (Appendix 2). From the spatial distribution maps (Figure 4:10), higher levels of salinity values were determined in several regions in the wet season compared to the dry season. This could be due to increased runoffs of salts and other pollutants into the springs.



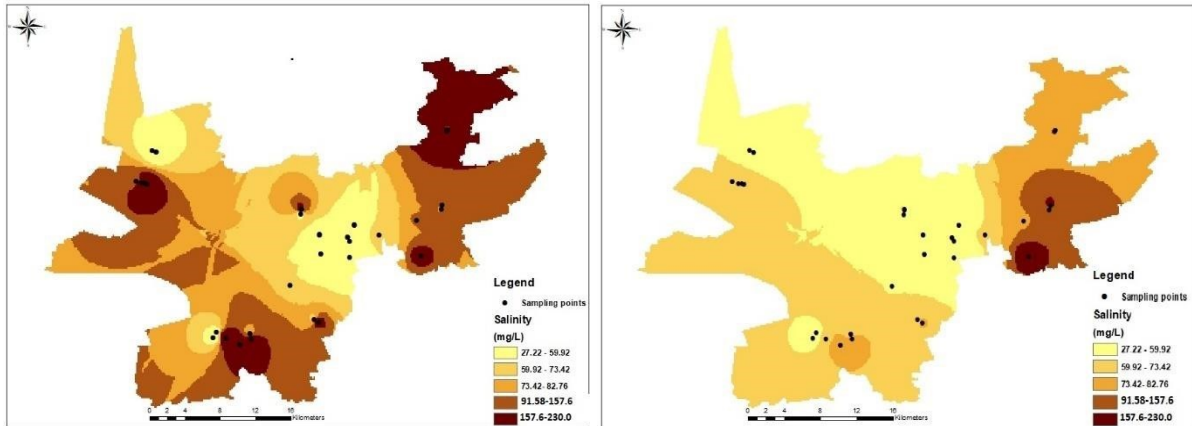


Figure 4.10: Spatial Distribution of salinity (A- wet season and B- dry season)

#### 4.1.6 Turbidity

According to the results, turbidity concentration ranged from 0- 8.24 NTU (dry) and 2.27- 18.88 NTU (wet) with means of  $1.39 \pm 0.4$  NTU and  $5.7 \pm 3.59$  NTU, respectively (Figure 4.11). The wet season recorded higher levels compared to the dry season as shown in (Figure 4.11). 36.58% (dry) and 100% (wet) values that exceeded the recommended of 1 NTU and <5 NTU prescribed by (SANS, 2015; WHO, 2011) respectively were recorded for domestic purposes but complied with the permissible limit for other uses, such as agriculture, aquaculture, and recreation (<25 NTU) (WHO, 2011) (Appendix 1). High turbidity could also have resulted from soil runoffs and untreated waste from sewage. The results obtained were comparable to those obtained by Makungo et al., (2018) which were within a range of 0.00 to 25.91 NTU. Another study by Odiyo et al. (2020) showed that turbidity of all the studied boreholes was in the range of 1–5 NTU indicating that they were within the required standard.

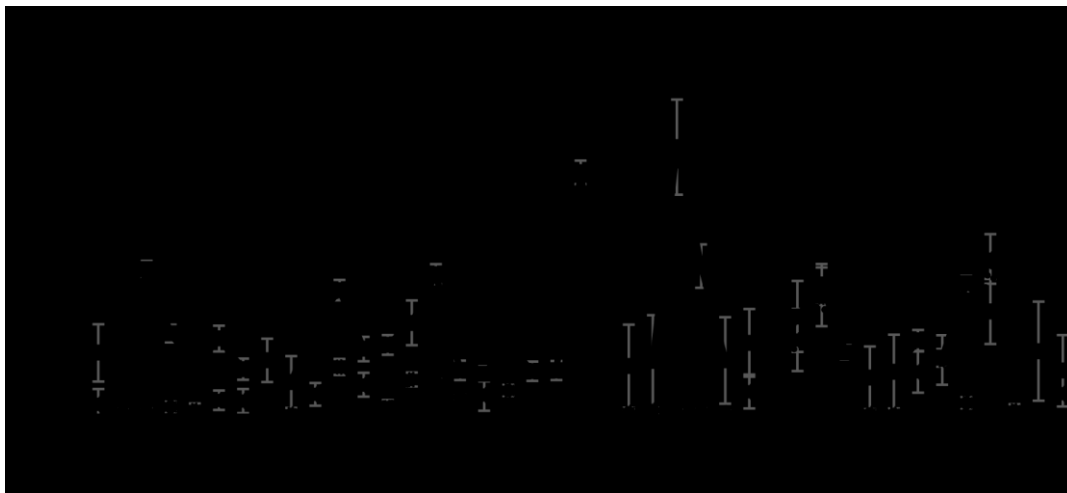


Figure 4.11: Turbidity variation in water samples

There was a significant difference in the means of the turbidity values obtained ( $p < 0.01$ ) between both seasons (Appendix 2); the spatial distribution of turbidity value ranges are shown in Figure 4.12. The maps show that turbidity values were more on eastern side and decreased towards the south-west in the wet season.

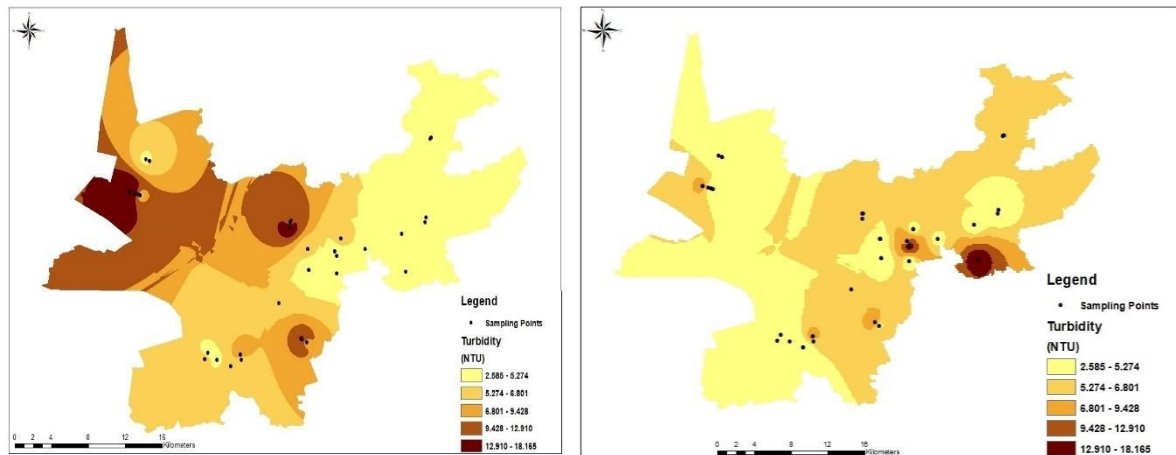


Figure 4.12: Spatial Distribution of Turbidity (A- wet season and B- dry season)

## 4.2 Chemical Water Parameters

### 4.2.1 Major Anions

Fluoride is considered very essential in water. However,  $< 0.5$  mg/l value can have negative effects on children; more than  $< 1.5$  mg/L level can be associated with skeletal fluorosis and dental problems, including non-fluorosis diseases (Onipe et al., 2020). The concentration of Fluoride recorded in all spring water points was at low levels and varied between detection limit of (BDL) - 0.187 mg/L (dry season) and BDL- 0.221 mg/L (wet season), with an average of  $0.088 \pm 0.002$  and  $0.086 \pm 0.001$ , respectively (Table 4.1); most of the sampled spring water recorded levels below the detection limit. All the spring water complied with the regulatory guidelines of WHO and SANS for domestic, agriculture, and livestock water purposes (SANS, 2015; WHO, 2011). Fluoride is known to be lethal in high doses and has negative side effects (Somasundaram et al., 2015; Sameer et al., 2011). Excessive fluoride exposure can be linked to several health issues, such as skeletal fluorosis, neurological problems, thyroid dysfunction, skin problems, high blood pressure, and heart failure (Radfarda et al., 2019). The results recorded showed that there was statistically no difference in average spring water levels of fluoride during the wet and the dry seasons ( $P > 0.05$ ) (Appendix 2). Results from this study are comparable to those reported by Packialakshmi et al., (2015) which ranged from 0.46- 0.56 mg/L.

The recorded level of  $Cl^-$  in spring water ranged from 2.81- 42.26 (dry) and 3.79- 45.97 mg/L (wet) with detected averages of  $10.4\pm 0.035$  mg/L (dry) and  $12.028\pm 0.145$  mg/L (wet). The highest and lowest values of  $Cl^-$  detected was 45.97 mg/L at S21 and 2.81 mg/L at S39 (Table 4.1). There was a presence of chloride in the water, however, the level was very low and complied with the regulatory standard guideline of SANS, DWAF, and WHO for domestic use, irrigation, livestock, and aquaculture (WHO, 2011, DWAF, 1996; SANS, 2015). Spatial distribution of chloride in Thulamela municipality was within the standard limit but in the northeast part was detected high value of chloride in both seasons (Figure 4.13).

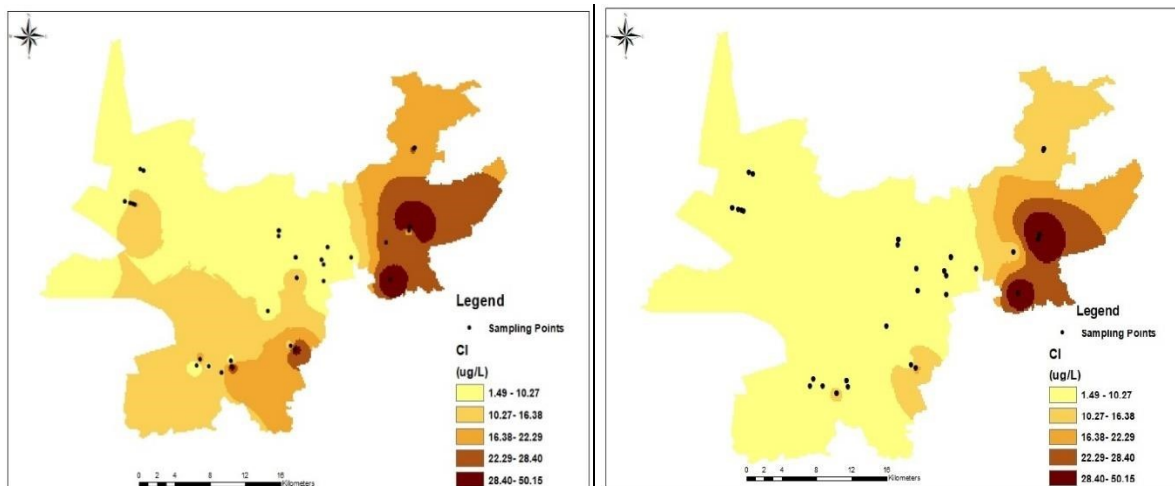


Figure 4.13: Spatial Distribution of  $Cl^-$  (A- wet season and B- dry season)

A study conducted, by (Nephalama and Muzerengi, 2016) in the Limpopo Province of South Africa showed high levels of  $Cl^-$  compared to this study. There was a significant positive correlation with  $Cl^-$  and  $NO_3^-$  with  $r=0.76$  (dry) and  $0.82$  (wet). This indicates a significant contribution from agricultural chemical residues (Islam et al., 2017).

The reported results of  $SO_4^{2-}$  ranged from BDL- 20.595 mg/L (dry) and BDL- 27.984 mg/L (wet) with recorded averages of  $5.73\pm 0.01$  mg/L and  $5.23\pm 0.07$  mg/L, respectively. None of the spring water exceeded the recommended limit set by (SANS, 2015; WHO, 2011) in drinking water and residential water uses of 200 and 250 mg/L (WHO, 2011; SANS, 2015) and irrigation purpose (1000 mg/L) set by DWAF (1996) (Table 4.1). These results are similar to those reported by Mudzielwana et al. (2020), where 100% of the samples were within the standard limit.

The concentration of  $PO_4^{3-}$  detected in the study ranged from BDL- 0.28 mg/L in the wet season whereas it was found to be BDL in all the spring samples in the dry season. All of the water complied with the standard set by (WHO, 2011 and SANS, 2015) in both studied seasons, except for S16, S17 and S18 in the wet season (Table 4.1).

The concentration of  $NO_2^-$  detected in all the observed springs varied from BDL- 0.18 mg/L (dry season) and BDL- 0.13 mg/L (wet season) with an average of  $0.09 \pm 0.04$  mg/L and  $0.13 \pm 0.06$  mg/L, respectively. The level of  $NO_2^-$  was very low in both seasons and complied with the recommended limit of  $\leq 0.9$  and 1 mg/L (SANS, 2015 and WHO, 2011). A study by Mukonazwothe et al. (2022) also showed low levels of nitrite.

The level of  $NO_3^-$  recorded, however, ranged from BDL- 56.53 mg/L (dry season) and 1.11- 51.1 mg/L (wet season) (Table 4.1). The averages found in the dry and wet seasons were 8.29 mg/L and 12.86 mg/L, respectively. Compared to other anions in the study,  $NO_3^-$  levels were higher which could be attributed to agricultural activities, and surface water runoffs in the study area. Most of the springs water fell within the threshold limit, 21.95% (dry) and 31.7% (wet) however, they exceeded the limit for drinking water and aquaculture (0 - 0.05) (Table 4.1; Appendix).  $NO_3^-$  gradually increased from the south-west to west parts of the Municipality, in the wet season, while in the dry season, it gradually increased from the southern to eastern parts (Figure 4.14).

Sample ID	Dry Season														Wet Season													
	F (mg/L)	Cl (mg/L)	SO4 (mg/L)	PO4 (mg/L)	NO2 (mg/L)	Br (mg/L)	NO3 (mg/L)	Na (mg/L)	Mg (mg/L)	P (mg/L)	K (mg/L)	Ca (mg/L)	HCO <sub>3</sub> <sup>-</sup> (mg/L)	F (mg/L)	Cl (mg/L)	SO4 (mg/L)	PO4 (mg/L)	NO2 (mg/L)	Br (mg/L)	NO3 (mg/L)	Na (mg/L)	Mg (mg/L)	P (mg/L)	K (mg/L)	Ca (mg/L)	HCO <sub>3</sub> <sup>-</sup> (mg/L)		
S1	0.049±0	9.87±0.118	BDL	BDL	BDL	0.048±0.0014	7.284±0.089	8.68±2.24	9.44±2.14	0.05±0	0.385±0.06	14.945±4.24	5.98877	0.051±0	9.6215±0.75	BDL	BDL	BDL	0.049±0.001	8.8355±4.06	8.705±0.68	8.165±0.48	BDL	0.255±0.05	14.72±1.32	10.13		
S2	0.056±0.0024	6.63±0.402	BDL	BDL	BDL	0.0475±0.0007	1.542±0.345	7.02±0.4	5.89±0.25	BDL	0.23±0	10.175±0.56	8.73469	0.054±0	6.494±0.57	BDL	BDL	BDL	BDL	1.511±1.65	7.5±0.07	6.15±0.30	0.04±0	0.24±0	11.695±0.88	16.541		
S3	BDL	4.511±0.044	BDL	BDL	BDL	BDL	0.625±0.151	5.83±0.56	6.645±0.53	BDL	0.215±0.02	11.82±0.53	6.58944	BDL	4.453±0.01	BDL	BDL	BDL	BDL	2.116±1.48	5.81±0.38	6.15±0.86	BDL	0.195±0.02	11.695±0.7	24.083		
S4	BDL	4.39±0.006	BDL	BDL	BDL	BDL	0.5065±0.004	5.78±0.08	5.021±0.02	BDL	0.225±0.01	10.525±0.53	6.58944	BDL	4.576±0.07	BDL	BDL	BDL	BDL	1.329±0.72	5.81±0.67	5.875±0.85	BDL	0.195±0.01	11.13±0.25	18.803		
S5	BDL	5.46±0.265	BDL	BDL	BDL	BDL	5.0875±1.019	4.75±0.32	3.885±0.47	BDL	1.16±0.61	4.905±0.81	6.33201	BDL	5.6575±0.34	BDL	BDL	BDL	BDL	5.526±1.63	5.775±0.43	3.915±0.45	BDL	0.65±0.06	5.31±0.86	21.066		
S6	BDL	4.48±0.6	BDL	BDL	BDL	BDL	0.9995±1.339	5.31±0.32	3.91±0.21	BDL	0.285±0.04	6.38±1.19	4.37210	BDL	5.6715±0.65	BDL	BDL	BDL	0.77±0	5.4245±2.11	6.45±1.66	4.16±1.55	BDL	0.325±0.063	7.7±3.1	21.066		
S7	BDL	4.49±0.035	BDL	BDL	BDL	BDL	1.1735±0.446	5.4±0.13	3.97±0.17	BDL	0.355±0.02	6.21±1.17	6.33201	BDL	6.397±1.71	BDL	BDL	BDL	BDL	8.1085±7.07	6.74±0.72	4.51±0.04	BDL	0.355±0.08	8.99±0.25	16.163		
S8	BDL	5.34±1.078	BDL	BDL	BDL	BDL	3.6365±2.986	8.73±3.75	7.545±5.01	BDL	0.45±0.11	9.07±5.01	4.4699	BDL	6.682±3.22	BDL	BDL	BDL	0.048±0	8.324±11.26	7.085±0.53	4.45±0.24	BDL	0.58±0.014	7.095±0.66	11.135		
S9	BDL	9.41±2.371	BDL	BDL	BDL	0.057±0	13.625±7.987	9.715±3.77	5.875±2.24	BDL	0.445±0.19	6.605±0.36	5.0877	BDL	10.582±6.28	1.85±0	BDL	BDL	0.066±	19.968±13.20	13.075±1.039	7.77±0.39	BDL	0.35±0.04	5.885±0.32	20.689		
S10	0.05±0.0014	8.942±0.212	BDL	BDL	BDL	BDL	6.156±0.015	7.72±0.13	6.88±0.06	BDL	0.195±0.21	11.67±0.17	4.100	0.0505±0.0007	9.3685±0.89	BDL	BDL	BDL	BDL	7.784±3.40	8.38±1.145	5.585±2.02	BDL	1.95±1.8	8.12±7.4	19.180		
S11	0.0655±0.0021	6.83±0.145	BDL	BDL	BDL	BDL	1.6345±1.271	9.215±0.47	5.985±0.05	BDL	0.3±0.06	10.605±0.19	5.817	0.0645±0.0035	12.571±4.65	2.084±0.395	BDL	BDL	0.065±0	11.935±6.90	10.545±1.16	7.185±1.63	BDL	0.29±0.056	15.03±3.9	19.784		
S12	0.0885±0.0021	20.84±0.452	2.653±0.051	BDL	BDL	0.074±0.0042	24.55±0.255	13.12±0.04	13.725±0.18	BDL	BDL	21.66±2.35	5.902	0.09±0.0014	25.4195±5.15	2.7895±0.083	BDL	BDL	0.0885±0.0134	34.71±14.25	14.7±2.82	16.58±4.31	BDL	0.28±0.141	28.145±7.6	14.655		
S13	0.072±0	11.46±0.274	3.485±0.223	BDL	BDL	BDL	5.294±1.461	13.31±0.13	12.42±0.59	BDL	0.68±0.03	12.505±1.42	6.2462	0.061±0.0042	19.578±1.57	8.318±5.83	BDL	BDL	0.0615±0.0007	39.23±13.07	17.59±2.88	16.775±0.86	BDL	0.91±0.028	19.6±1.54	16.541		
S14	0.0785±0.0035	5.60±0.083	BDL	BDL	BDL	BDL	0.083±0.4	8.535±0.02	8.6±0.16	BDL	0.35±0.06	13.875±0.25	6.9326	0.068±0.0085	8.692±1.34	BDL	BDL	BDL	0.047±0	6.493±7.12	6.765±2.01	7.025±2.38	BDL	0.395±0.035	12.59±4.53	16.541		
S15	0.0765±0.0021	5.61±0.496	BDL	BDL	BDL	BDL	0.6945±0.22	9.36±2.09	9.22±1.58	BDL	0.575±0.08	17.285±3.29	5.5425	0.0665±0.0049	8.0735±2.4	BDL	BDL	BDL	0.048±0	5.55±7.44	8.345±0.38	9.025±2.17	BDL	0.5±0.197	16.185±3.24	24.460		
S16	0.1685±0.012	14.83±0.286	BDL	BDL	0.065±0	0.0575±0.0035	2.064±2.66	14.035±0.36	12.81±0.10	0.155±0.21	1.175±0.06	17.515±0.33	4.65871	0.1575±0.0049	14.615±0.51	1.601±0.024	0.2845±0.037	BDL	0.061±0.0028	16.269±1.82	14.61±0.48	13.155±0.89	0.16±0.014	1.37±0.24	20.565±1.47	15.792		
S17	0.1605±0.1181	9.39±5.262	BDL	BDL	BDL	BDL	2.837±0	16.66±1.37	14.705±1.77	0.195±0.02	1.36±0.10	20.385±2.28	7.30423	0.158±0.0042	14.637±0.24	1.589±0	0.142±0.0311	BDL	0.0605±0.0021	15.371±2.64	13.845±0.37	13.07±0.07	0.145±0.02	1.17±0.028	19.225±0.05	18.803		
S18	BDL	4.4835±5.158	BDL	BDL	BDL	BDL	0.6285±0.09	6.95±0.16	4.09±0.14	0.165±0	1.735±0.01	6.12±0.01	7.79078	0.108±0.0028	4.411±0.39	BDL	0.2275±0.0547	BDL	BDL	3.734±2.23	7.2±0.48	4.055±0.04	8.9825±0.01	2.26±0.20	8.295±1.72	21.443		
S19	0.087±0.0014	7.4915±0.383	BDL	BDL	0.076±0	BDL	5.33±1.64	8.61±0.45	5.02±0.35	BDL	1.2±0.06	7.725±0.45	7.44754	0.0745±0.012	9.9045±2.97	BDL	BDL	BDL	0.055±0	20.762±8.34	9.825±1.03	5.9±0.86	BDL	1.21±0.042	11.325±1.88	21.443		
S20	0.0625±0.0021	19.2615±1.266	3.368±0.068	BDL	BDL	0.076±0.0042	25.366±1.338	13.625±0.32	19.14±0.81	BDL	0.26±0.07	27.87±4.02	8.24557	0.06±0	21.65±0.51	4.1195±0.729	BDL	BDL	0.0805±0.009	30.727±6.24	14.125±0.11	18.29±2.63	BDL	0.385±0.22	31.765±0.64	19.180		
S21	0.1865±0.007	38.918±1.206	20.5955±0.759	BDL	0.181±0	0.122±0.0057	37.156±0.46	23.59±0.08	42.3±0.45	BDL	0.39±0.06	50.81±4.57	6.16039	0.221±0.0141	45.97±5.57	27.984±3.736	BDL	BDL	0.13±0.113	36.425±1.24	28.685±3.44	46.955±1.08	BDL	0.42±0.11	59.75±1.95	22.801		
S22	0.0915±0.007	35.804±4.245	6.1615±0.648	BDL	BDL	0.087±0.0028	0.763±0.643	18.48±1.41	27.585±0.62	BDL	0.36±0.10	41.215±4.57	3.2867	0.0865±0.0106	29.839±0.66	6.3635±1.377	BDL	BDL	0.09±0.024	14.24±15.62	19.29±1.47	25.04±1.23	BDL	0.415±0.035	39.11±4.6	23.329		
S23	0.0675±0.0021	42.267±3.541	4.2655±0.292	BDL	BDL	0.112±0.0028	56.525±1.67	18.7±0.03	31.25±0.64	BDL	0.2±0	42.765±2.43	2.3847	0.0695±0.049	45.6385±3.8	4.033±0.989	BDL	BDL	0.1155±0.0021	51.10±31.80	18.64±0.84	29.84±0.54	BDL	0.275±0.10	46.48±3.8	22.574		
S24	0.061±0	14.2355±0.292	3.1575±0.011	BDL	BDL	0.06±0.009	25.021±1.32	12.225±0.12	18.72±0.66	BDL	0.33±0.03	29.78±1.10	4.7874	0.0645±0.0007	14.7005±0.23	3.3395±0.081	BDL	0.129±0	0.077±0.099	24.555±2.27	12.635±0.08	18.795±0.44	BDL	0.3±0.06	33.075±2.8	19.407		
S25	BDL	7.234±0.093	BDL	BDL	BDL	0.059±0	4.084±0.163	7.355±0.60	7.68±0.61	BDL	0.34±0	10.79±1.77	3.1853	BDL	7.227±0.05	BDL	BDL	BDL	0.0565±0.0007	5.504±0.28	7.32±0.56	7.505±0.04	BDL	BDL	11.78±0.10	19.407		
S26	BDL	10.582±0.536	BDL	BDL	BDL	0.051±0	13.4515±5.66	7.775±0.36	11.275±1.15	BDL	0.295±0.04	16.67±1.12	5.6455	BDL	9.4215±0.17	BDL	BDL	BDL	0.057±0.00141	19.063±6.02	7.625±0.11	10.385±0.32	BDL	BDL	16.955±1.67	18.803		
S27	BDL	10.2125±1.027	BDL	BDL	BDL	0.05±0.0014	13.9145±4.79	6.15±0.61	9.16±1.02	BDL	0.575±0.28	11.99±5.43	4.9590	BDL	8.4815±1.3	BDL	BDL	BDL	0.0525±0.0035	12.052±1.69	7.505±0.46	9.555±0.86	BDL	0.32±0	15±1.05	22.574		
S28	BDL	6.6575±0.086	BDL	BDL	BDL	BDL	8.578±0.139	6.15±1.34	4.795±0.47	BDL	0.325±0.01	7.66±1.03	7.1043	BDL	7.683±2.53	BDL	BDL	BDL	0.057±0	8.829±2.71	5.29±0.22	4.24±0.41	BDL	0.31±0.07	7.9±1.11	12.392		
S29	BDL	6.3865±0.139	BDL	BDL	BDL	BDL	9.4845±0.043	5.56±0.10	4.98±0.10	BDL	0.375±0.01	8.18±0.38	7.9624	BDL	6.29±1.02	BDL	BDL	BDL	BDL	5.823±2.81	6.8±0.05	6.82±7.1	BDL	0.45±0	11.99±13.63	21.44		
S30	BDL	3.4785±0.405	BDL	BDL	BDL	BDL	1.976±1.134	4.6±1.61	1.95±0.74	BDL	BDL	2.635±0.49	6.731	BDL	5.549±0.85	BDL	BDL	BDL	BDL	6.998±0.17	5.22±0.73	3.555±2.26	BDL	0.41±0	6.2±5.06	20.312		
S31	BDL	3.403±0.173	BDL	BDL	BDL	BDL	BDL	3.6±0.03	1.36±0.13	0.04±0	0.18±0	2.135±0.59	6.246	BDL	5.323±0.92	BDL	BDL	BDL	BDL	5.881±0.03	4.66±0.71	1.77±0.084	0.04±0	0.73±0	3.405±0.34	22.574		
S32	BDL	3.231±0.006	BDL	BDL	BDL	BDL	1.91±0.054	3.19±0.18	1.135±0.10	BDL	BDL	1.61±0.24	7.0184	BDL	3.797±0.22	BDL	BDL	BDL	BDL	4.555±3.34	4.785±1.12	3.525±3.16	0.21±0	2.73±0	3.41±1.30	19.558		
S33	BDL	8.6975±4.201	BDL	BDL	BDL	BDL	4.65±0.539	6.41±4.61	2.005±1.15	BDL	BDL	2.77±1.92	6.503	BDL	9.80±5.32	BDL	BDL	BDL	0.05±0	8.942±4.57	7.355±2.62	2.685±0.67	BDL	BDL	4.71±1.42	18.803		
S34	BDL	11.6545±0.015	BDL	BDL	BDL	0.05±0	24.65±0.03	9.55±1.22	6.845±0.57	BDL	0.19±0	6.93±0.04	6.546	BDL	10.73±0.91	BDL	BDL	BDL	0.051±0	21.449±2.84	10.145±2.22	10.005±5.33	BDL	BDL	13.545±8.72	15.78		
S35	BDL	8.0405±0.06	BDL	BDL	BDL	BDL	5.96±0.885	5.575±0.11	3.875±0.12	BDL	BDL	2.74±0.05	4.838	BDL	8.59±0.21	BDL	BDL	BDL	BDL	11.821±14.28	5.615±0.06	4.615±0.95	0.06±0	BDL	4.08±0.32	22.197		
S36	BDL	8.2775±0.105	BDL	BDL	BDL	BDL	5.63±1.008	5.26±0.07	3.64±0.01	BDL	0.2±0	2.74±0.45	0.582	BDL	8.88±0.54	BDL	BDL	BDL	BDL	10.549±13.25	5.25±0.74	3.89±1.79	BDL	BDL	4.87±0.68	22.952		
S37	0.0815±0.0191	9.555±3.749	2.207±0.692	BDL	BDL	0.059±0	2.65±0.725	17.14±0.71	12.605±0.25	BDL	0.435±0.06	23.03±0.66	5.782	0.0805±0.0007	12.693±0.71	3.335±1.236	BDL	BDL	0.062±0.007	7.428±0.98	18.72±0.09	13.3±0.42	BDL	0.385±0.05	27.795±0.21	22.046		
S38	BDL	9.817±3.439	BDL	BDL	BDL	0.053±0	3.70±1.877	8.42±1																				

WHO (2011)	1	250	200	0.03	<1	0.1	10	300	30-150	10	20	200	150	1	250	200	0.03	<1	0.1	10	300	30-150	10	20	200	150
SANS (2015)	≤ 1.5	≤ 300	≤ 250	<0.03	≤ 0.9	0.1	≤ 11	200	70	10	50	150	>150	≤ 1.5	≤ 300	≤ 250	<0.03	≤ 0.9	0.1	≤ 11	200	70	10	50	150	>150

**Table 4.1:**

Mean concentrations and standard deviation of the Anions and major cations in spring water

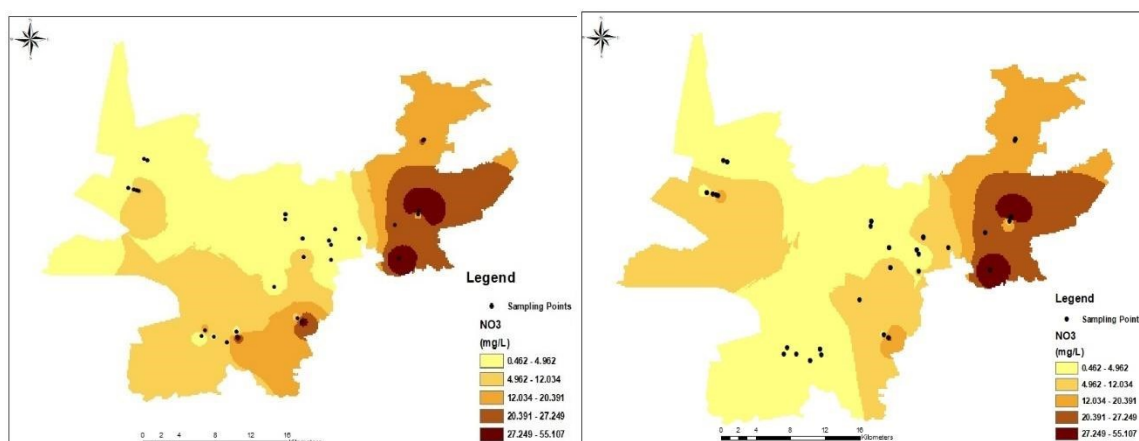


Figure 4.14: Spatial Distribution of  $NO_3^-$  (A- wet season and B- dry season)

$NO_3^-$  in spring water, frequently resulted from, agricultural activities, industrial pollution, surface water runoffs, manures, or improper disposal of human and animal waste (Bouchard et al., 1992; Soleimani et al., 2020). The concentration recorded can be compared to a study by Molekoa et al. (2019) showed that some locations exceeded the threshold limit.

The concentration of  $HCO_3^-$  ranged from 0.58- 8.73 mg/L (dry) and 10.13- 25.21 mg// (wet) with average and standard deviation of  $8.7 \pm 1.81$  and  $19.14 \pm 3.9$ , respectively. The possible sources of  $HCO_3^-$  include the presence of organic matter in the study area, that is oxidized to produce carbon dioxide and which also promotes dissolution of minerals;  $HCO_3^-$  may result from dissolution of  $CO_2$  in rain and weathering of silicate rocks Dube et al. (2020). The current results were comparable to those obtained by Durowoju et al. (2019) which fell within a range of 39.6 to 152.5mg/L.

The levels of Br determined in this study ranged from BDL- 0.122 mg/L (dry) and BDL- 0.13 mg/L (wet) with the average of  $0.0674 \pm 0.004$  mg/L and 0.094 respectively. 95% of the springs analyzed fell within regulated threshold set by (SANS, 2015; WHO, 2011) except for S1 and S23 in both seasons (Table 4.1). The results of this study are comparable to a study reported by Onipe et al. (2020) conducted at spring water of Siloam area, Limpopo Province, South Africa.

Most of the recorded values of anions showed that there was no statistical difference in average spring water levels of  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$  during the wet and the dry seasons ( $P > 0.05$ ), with recorded p values of  $Cl^-$  (0.432);  $SO_4^{2-}$  (0.93) and  $NO_3^-$  (0.083) (Appendix 2).

#### 4.2.2 Major Cations

The observed concentration of K in the dry season ranged from BDL-1.735 mg/L and BDL2.73 mg/L for the wet season (Table 4.1). The averages recorded were  $0.501 \pm 0.02$  mg/L (dry) and  $0.62 \pm 0.06$  mg/L (wet). All of the studied samples of spring water complied with the recommended level for domestic purposes (WHO, 2011 and SANS, 2015). Lulambe and Kanyerere. (2022) reported potassium levels in water in Soutpansberg Region, Limpopo Province, which were higher than the levels recorded in this study. The levels of sodium in groundwater should not be high as it would increase the salinity and conductivity levels of the water. In this study, the average level of Na recorded in the dry season ranged from 3.19 – 23.59 mg/L with an average of  $9.06 \pm 4.65$  and 4.66- 28.68 with average of  $9.70 \pm 5.13$  mg/L in the wet season, respectively. They both fell within the recommended guideline and complied with the regulatory standards for domestic, aquaculture, and agricultural and recreation uses (WHO, 201; SANS, 2015). Figure 4.15 shows the spatial distribution of Na in the Thulamela area in both seasons. Higher concentration of Na were present in the eastern part of the study area in both seasons, due to activities as agriculture practiced in the area leading to fertilizers being deposited in spring water (Figure 4.15). The results obtained in this study are comparable to those reported by Madilonga et al. (2021) with Na levels within the range of 9.08–17.55 mg/L.

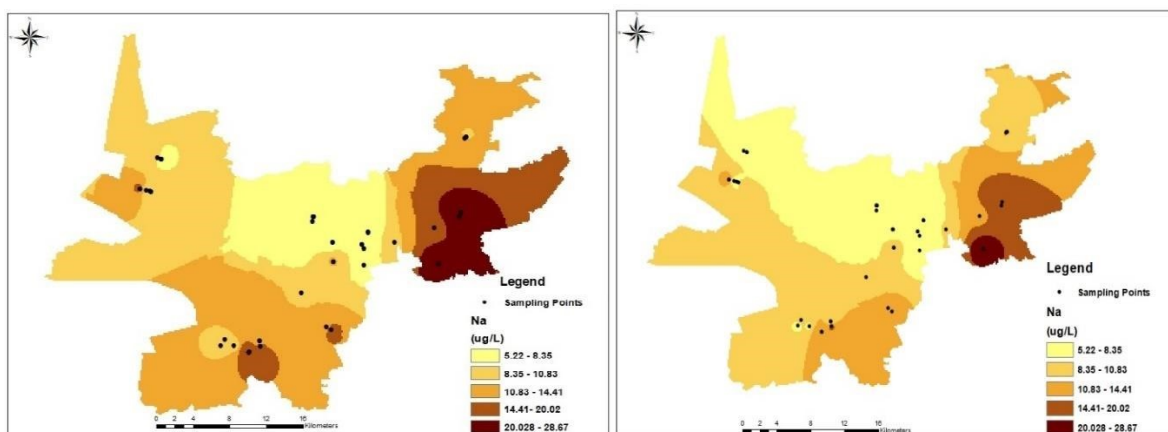


Figure 4.15: Spatial Distribution of Na (A- wet season and B- dry season)

Mg levels recorded ranged from 1.135- 31.25 mg/L in the dry season and 2.685-46.955 mg/L in the wet season (Table 4.1). The averages observed were  $9.21 \pm 8.75$  mg/L (dry) and  $9.74 \pm 8.55$  mg/L (wet). Higher levels of Mg were recorded in the wet season than in the dry season. The levels of Mg complied with the recommended guideline for domestic, recreation, and agricultural water use set by WHO (2011) and SANS (2015). The spatial distribution of Mg showed that the concentration increased from the south-west to the east parts. The



northern side recorded the lowest concentration (Figure 4.16). Also, a similar trend was determined in all the sampling sites, both in the wet and dry seasons. An excess of magnesium can cause effects, such as nausea diarrhoea and stomach cramps (Shigut et al., 2017, Amanial, 2015). The correlation between magnesium and other parameters are presented in Appendices 5 and 6. The levels recorded in this study could be compared to that of Makungo and Odiyo (2018) at Siloam Village, Limpopo Province.

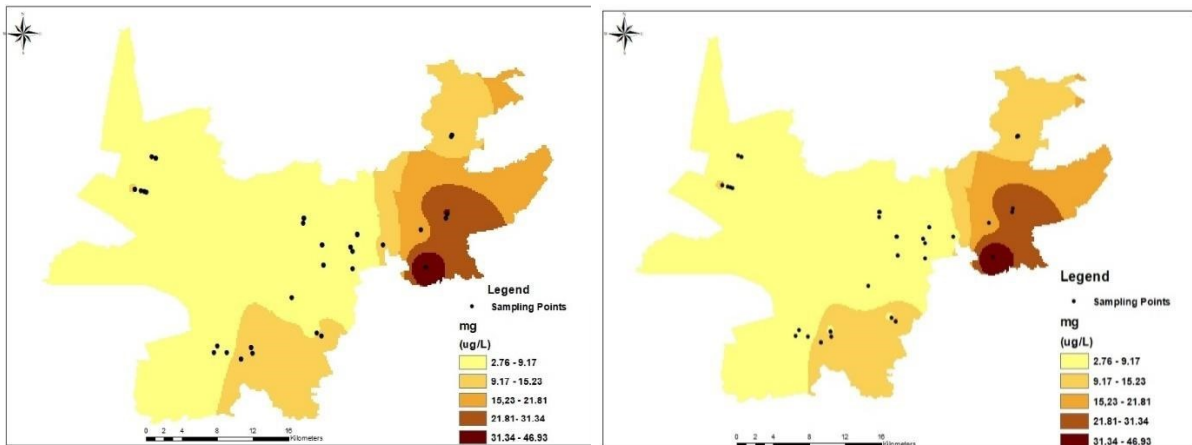


Figure 4.16: Spatial Distribution of Mg (A- wet season and B- dry season)

The concentration of Ca detected in the study, in the dry season ranged from 1.61-2.035 mg/L and 2.435-46.48 mg/L in the wet season. The averages recorded were  $12.9 \pm 11.5$  mg/L (dry) and  $14.25 \pm 12.42$  mg/L (wet); these complied with several recommended guideline for domestic, aquaculture, livestock and agricultural water use (WHO, 2011, SANS, 2015) (Table 4.2). Positive correlation was observed between Ca and Cl,  $\text{NO}_3$ , V and Sr for both seasons (Appendix 5 and 6). The spatial distribution map below, showed similar trends in both seasons (Figure 4.17). A study conducted by Elumalai et al. (2020) showed a comparable results to this study.

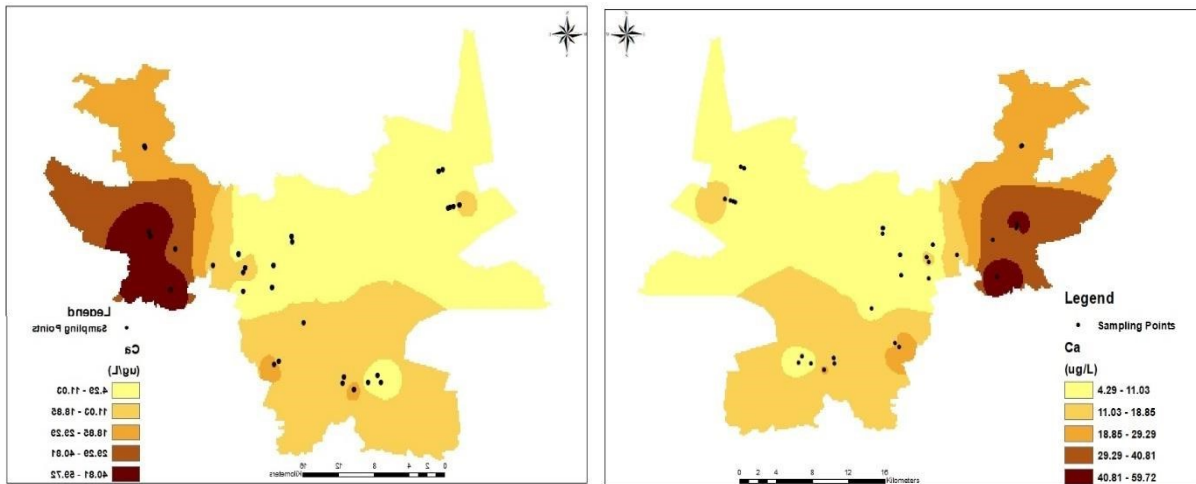


Figure 4.17: Spatial Distribution of Ca (A- wet season and B- dry season)

The results showed that there was no statistical difference in the mean of all studied major cations levels of the spring water during the wet and the dry seasons ( $P > 0.05$ ) (Appendix 2).

### 4.3 Hydrochemistry of the studied springs at Thulamela Municipality

#### 4.3.1 Piper plot

The Piper diagram revealed three hydro-chemical facies, for both seasons, Ca-HCO<sub>3</sub> type 1 (6% on dry and 78% on wet), mixed water type Ca-Mg-Cl type 4, (54% on dry and 12% on wet) and Ca-Cl<sub>2</sub> type 5 (40% dry and 10% wet) (Figures 4.18 and 4.19). It is suggested that the chemistry of the groundwater was controlled by a mixing and cation exchange processes (Ahmed et al., 2010). As observed from the Piper diagram, the Ca-HCO<sub>3</sub> water type, which was formed as a result of the reverse ion exchange of Ca-Cl waters, made Ca the dominant cation and HCO<sub>3</sub> the dominant anion; this resulted in the water's content of Ca-HCO<sub>3</sub>. The geochemical facies in the Piper chart uphold the strength of basic earth metals (Ca and Mg) which surpass the alkali metals (Na and K), and the strong acids (Cl and SO<sub>4</sub>) as well as exceeding the weak alkaline (HCO<sub>3</sub>). The weathering of silicate prevails in the interaction of rock water which are the essential variables for expansion in the significant ions' values in the groundwater. The findings of this study is similar to the studies revealed by Lulambe et al. (2022) and Onipe et al. (2021). A study conducted by Durowoju et al. (2019), however, contradicts these results as it reported that the Piper diagram of the geothermal spring water fell in the Na-Cl water type, excluding (SAW-WT29 and WT30) fell in water type Na-HCO<sub>3</sub> which was due to underlying geology emanating from rocks gneissic (NaCl) and basalt rocks (Na-HCO<sub>3</sub>).

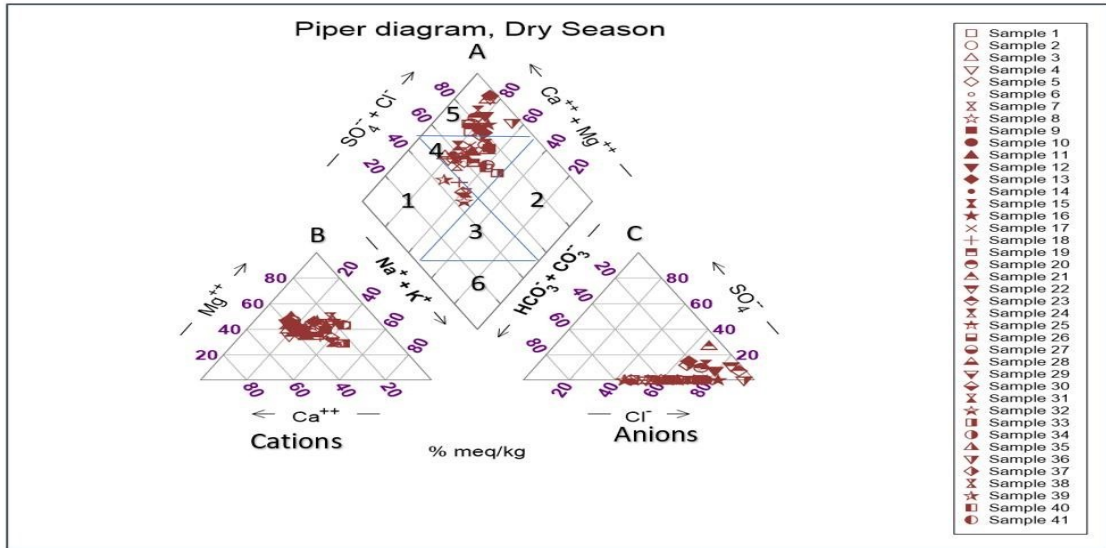


Figure 4.18: Piper diagram of spring water at Thulamela Municipality for dry season

1: Ca-HCO<sub>3</sub> type 2: Na-Cl type 3: Mixed Ca-Na-HCO<sub>3</sub> type 4: Mixed Ca-Mg-Cl type 5: Ca-Cl type 6: Na-HCO<sub>3</sub> type

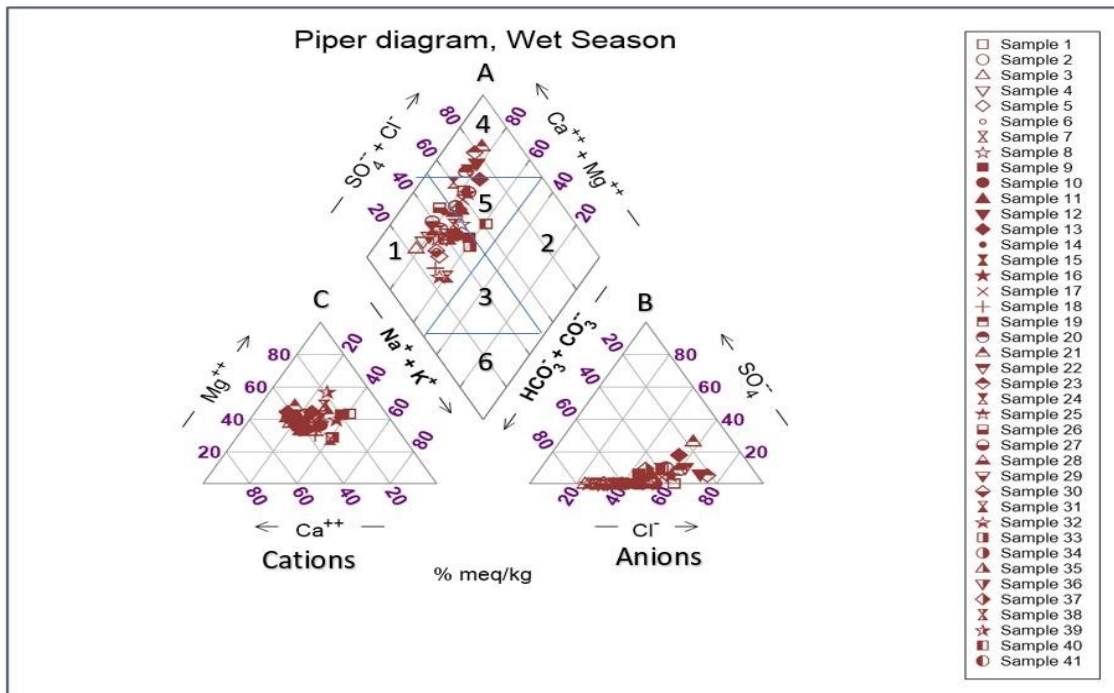


Figure 4.19: Wet season Piper diagram of spring water at Thulamela Municipality

### 4.3.2 Durov Plot

The findings from the Piper chart were validated with a Durov's plot to enable comprehension of the geochemical processes prompting different water types. To compute the

hydrochemical cycles domain and types of particle exchange synthetic data of groundwater spring water, samples was plotted on the Durov diagram (Durov, 1948). The Durov diagram supported the findings from the Piper diagram (Figures 4.20 and 4.21). The mixed-water type was dominant in the study area at 85%. The Durov's plot showed that majority of samples fell within the mixing zone and simple dissolution for both wet and dry seasons of water type Ca-Mg-Cl (Okogbue and Ukpai, 2013). Additionally, there were a few spring water samples that showed Ca and Cl as dominant cation and anion respectively, indicating that the groundwater may be related to reverse ion exchange of Ca-Cl waters. Groundwater aquifer were also dominated by Ca and  $\text{HCO}_3$  from reverse ion exchange, consequently making Ca- $\text{HCO}_3$  water type. The major water types found in the study were Ca-Mg-Cl (gypsum groundwater's), Ca-Cl (mine drainage and shallow) and Ca- $\text{HCO}_3$ , (fresh ground waters) influenced by ion-exchange processes. The results found in this study are comparable to those obtained by Lalumbe et al. (2022) and Durowoju et al. (2018).

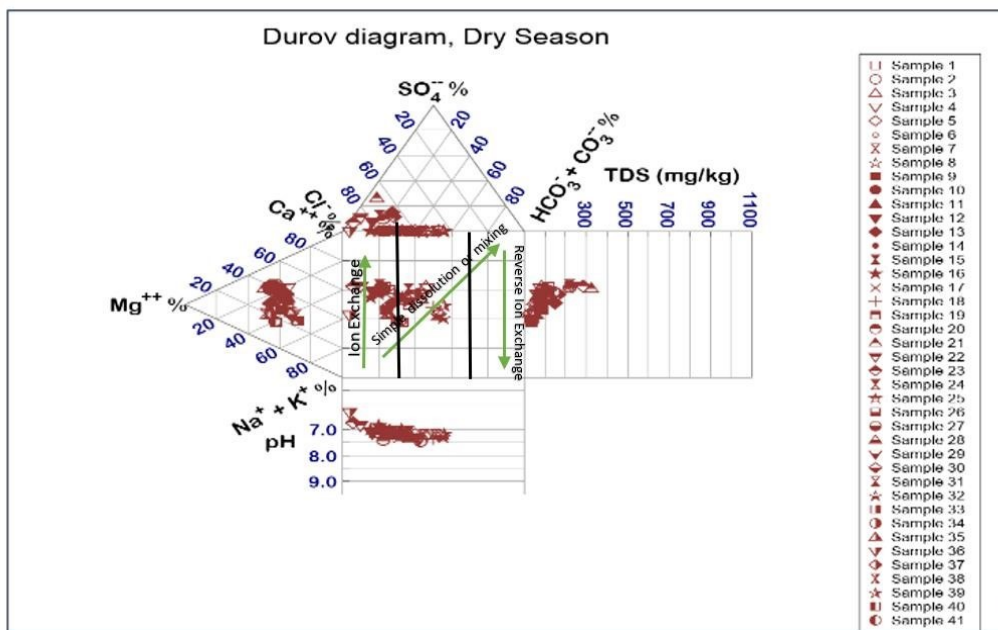


Figure 4.20: Durov diagram for dry season of spring water at Thulamela Municipality

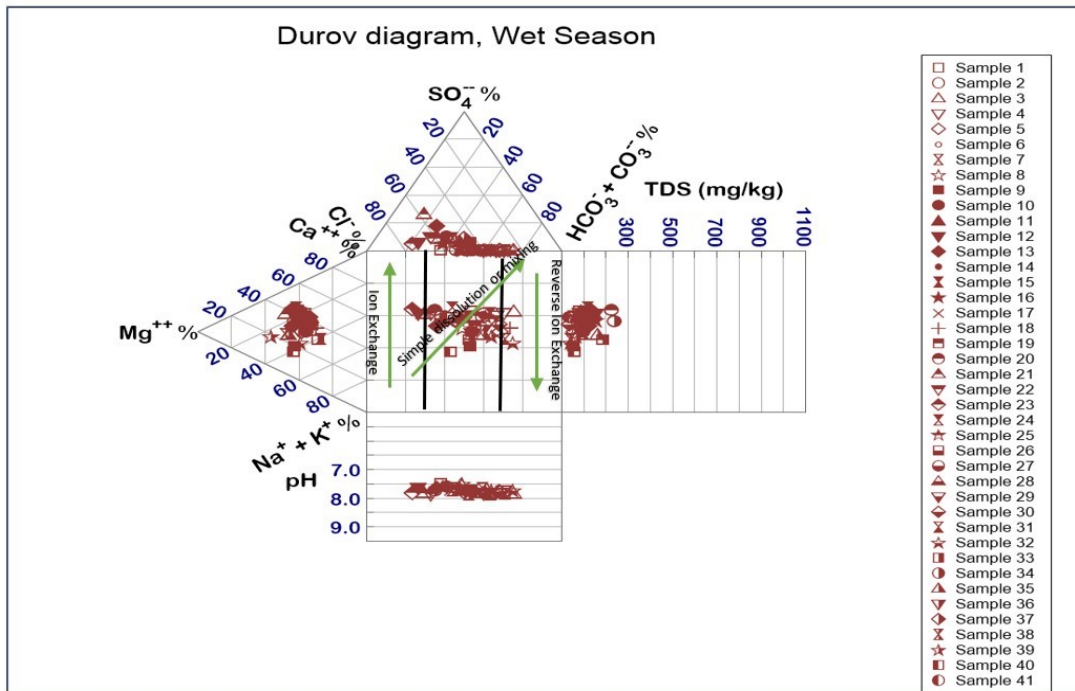


Figure 4.21: Durov diagram for wet season of spring water at Thulamela Municipality

### 4.3.3 Gibbs Plot

The Gibbs diagram is widely used to establish the relationship of water composition and aquifer lithological characteristics (Gibbs, 1970). Three distinct fields - precipitation dominance, evaporation dominance and rock–water interaction dominance (weathering) - constitute the segments in the Gibbs diagram controlling groundwater systems by plotting the TDS against  $Na/(Na+ Ca)$  and  $Cl/(Cl + HCO_3)$ . The spring water samples from Thulamela Municipality for all seasons fall in both weathering (the rock–water interaction) dominance and evaporation dominance field (Figure 4.22 and 4.23). Gibb's diagram (Figure 4.22) on groundwater of the study area, for the dry season, showed that the hydrogeochemical processes were mainly controlled by weathering with approximately 66% rock dominance, followed by evaporation dominance at 34%, whereas the wet season also showed that weathering of the aquifer material was the dominant process controlling the chemistry of the springs with 56% rock dominance and 44% evaporation dominance (Kumar et al., 2009) (Figure 4.22 and 4.23). In both seasons, however, weathering was the dominant process controlling the chemistry of the springs at Thulamela Municipality. These results are comparable to studies by Rambuwani et al. (2020); Ravikumar et al. (2015), Durowoju et al. (2019) which showed that the spring water/groundwater samples in the study area were controlled by the interaction of rock water. Durowoju et al., (2019) further stated that the dominant process that was controlling the chemistry of groundwater was weathering of the

aquifer. It is important to note that, the reactions of the chemicals vary spatially and temporally, relying upon formation of the geology, the compound nature of the underlying water, and residence time.

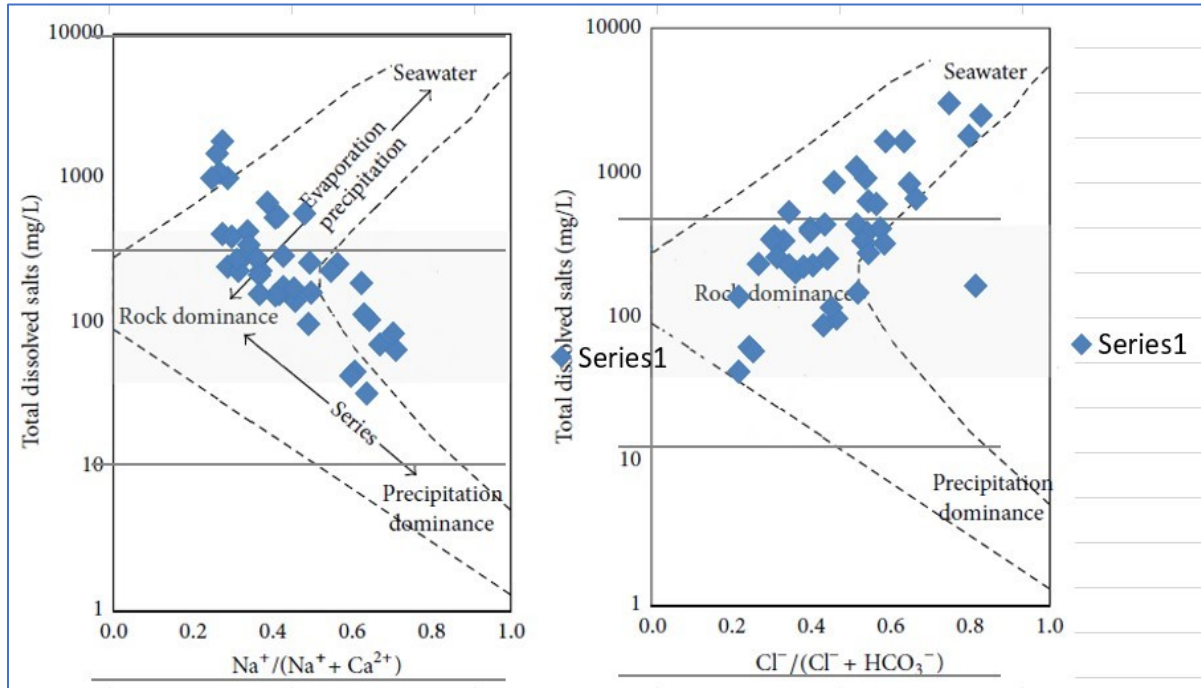


Figure 4.22: Gibbs plot showing the mechanism controlling the chemistry of the spring water for dry season

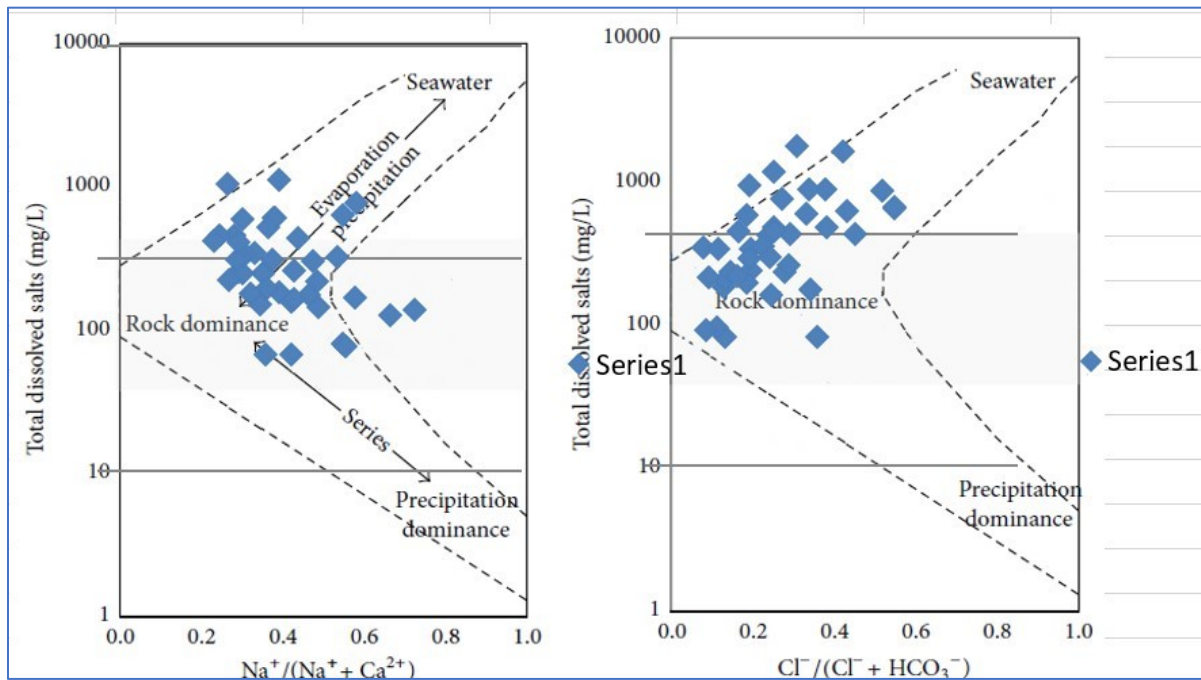


Figure 4.23: Gibbs plot showing the mechanism controlling the chemistry of the spring water for wet season

#### 4.4 Trace elements' concentrations in the spring water in Thulamela Municipality

The mean concentrations of 20 trace elements (Al, V, Mn, Fe, Co, Ni, Cu, Zn, Cr, As, Se, Sr, Mo, Cd, Sn, Sb, Ba, Hg, Pb, and Si) in the water samples were low; 98% of them complied with the standard guideline of WHO (2011) and SANS (2015). The results, however, indicated that there was a presence of some trace elements in the spring water of Thulamela Municipality which can have negative effects on human health. The average concentrations of Boron (B) in drinking water differed depending on the sampling site. The levels of B from all sampling points ranged from 5.53- 26.27  $\mu\text{g/L}$  in the dry season (Appendix 3) and 15.5 - 47.2  $\mu\text{g/L}$  in the wet season (Appendix 4). The averages found were  $13.23 \pm 6.74 \mu\text{g/L}$  (dry) and  $17.86 \pm 6.704 \mu\text{g/L}$  (wet). The standard guideline of Boron is 2400  $\mu\text{g/L}$  for drinking water, set by SANS (2015) and 5000  $\mu\text{g/L}$  set for livestock and irrigation purposes. The levels in the dry season were lower compared to the wet season, although, they did not exceed the limit. In addition, the spatial distribution of Boron in Thulamela showed higher levels in the western and eastern parts, than in the southern and northern parts (Figure 4.24). A high concentration of Boron in water can cause danger to the testicles of young boys and stomach cramps in adults. Patience et al. (2021) conducted a study that showed lower levels of B compared to this study, and fell within the regulatory guideline.

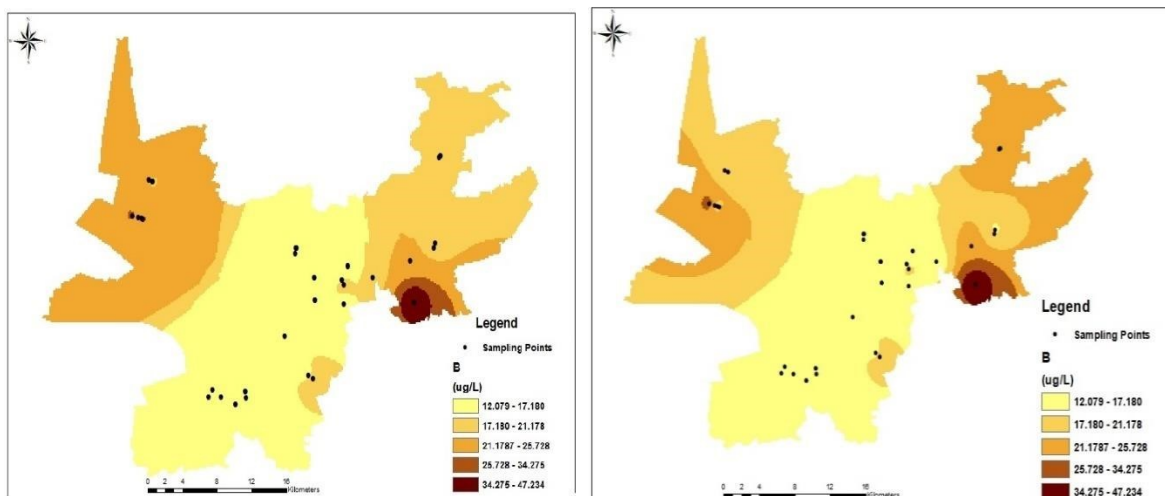


Figure 4.24: Spatial Distribution of Boron in spring water of TM (A- wet season and B- dry season)

The concentration of Cr ranged from 18.99 - 45.4  $\mu\text{g/L}$  in the dry season, while in the wet season it varied between 29.8-53.02  $\mu\text{g/L}$  with averages of  $36.4 \pm 5.26 \mu\text{g/L}$  and  $41.069 \pm 5.50 \mu\text{g/L}$ , respectively (Appendix 3 and 4). The standard guideline for Cr in drinking water is 50  $\mu\text{g/L}$  (SANS, 2015). In the dry season, 100% of the spring water fell within the standard limit set by SANS, (2015) and WHO (2011) (Appendix 3 and 4). In the wet season, Cr levels were, however, slightly higher compared to the dry seasons with 9.75% of springs water that failed

to comply with the standard guideline for domestic purposes but complied with (0-1000 µg/L) for livestock, irrigation, and 200 µg/L aquaculture purposes (WHO, 2011). Sewage and inappropriate disposal of waste observed in the area could have added to the level of Cr recorded. The spatial distribution shows that there was a higher concentration of Cr on the northwest side (Figure 4.25). Use of spring water with a high concentration of Cr has a potential negative impact on health, such as harming of the liver, kidney, possible lung cancer, allergic dermatitis, death, and irritation of the skin (Tanjung and Hamuna, 2019). The results indicated that the difference in the average of Cr for dry and wet seasons was significantly different ( $p < 0.05$ ) (Appendix 2). A study by Durowoju et al. (2019) reported the presence of Cr in spring water within Limpopo Province; they noted that it contributed mainly to ill-health. A study done by Olivier et al., (2011) at Siloam showed lower levels of Cr, in the range of 0.97 and 0.70 µg/l but within the standard guideline.

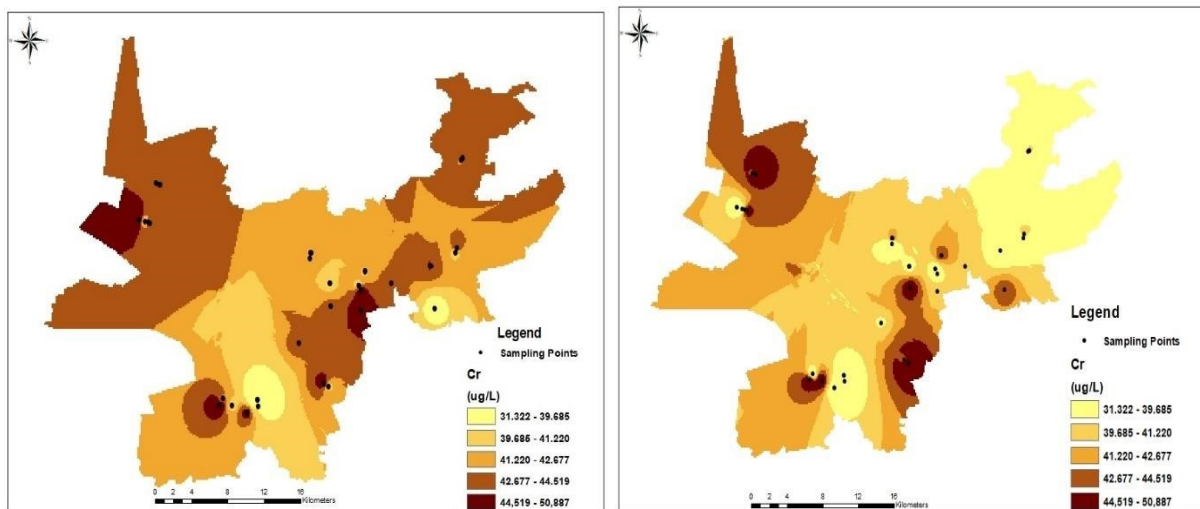


Figure 4.25: Spatial Distribution of Cr (A- wet season and B- dry season)

The level of As found in all sampling points in the dry season ranged from 0.06-0.3 µg/L and 0.07-0.515 µg/L in the wet season. The averages recorded were 0.095 µg/L ± 0.044 (dry) and 0.125 ± 0.076 µg/L (wet) (Appendix 3 and 4). From all sampled spring points at Thulamela Municipality, all the values were within the accepted range of no-health risk as proposed by WHO at 10 µg/L for drinking water (WHO, 2011; SANS, 2015). The statistical recorded results showed that the difference in the means of As for dry and wet seasons was significantly different ( $p < 0.05$ ) with a p-value of 0.0497 (Appendix 2). The fact that As is present in the water and the possible bio-accumulation of it in the human/animal body systems could result in a negative impact on their wellbeing, if ingested for a long period (Sinha and Prasad, 2020). Figure (4.26) shows the spatial distribution of As in the study area. Being exposed to arsenic may increase the danger of malignant or cancer growth, and damage to the kidney, bladder, skin liver, and bone (Chung and Hong, 2014). The study by Edokpayi et al. (2018) reported



lower values than was recorded in this study at Muledane area of Vhembe District, Limpopo Province, which complied with the standard guideline for drinking water.

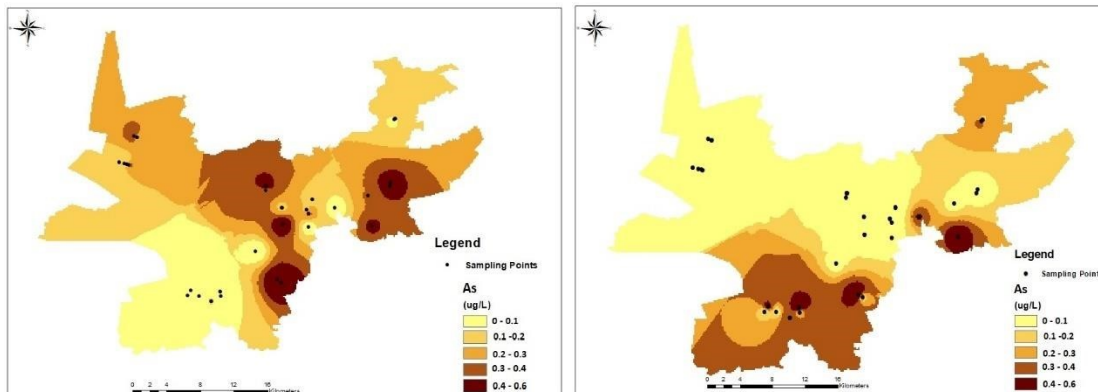


Figure 4.26: Spatial Distribution of As (A- wet season and B- dry season)

Se results in this study mostly showed BDL in both seasons. In general, there was no discernible difference between Se levels in the dry season as compared to the wet season. The concentration of Se in Thulamela Municipality's studied springs ranged from bdl-0.605 µg/L in the dry season and bdl-0.605 µg/L in the wet season with averages of  $0.4275 \pm 0.25102$  µg/L (dry) and  $0.397 \pm 0.293$  µg/L (wet). All the samples complied with the standard guideline considered safe for drinking purpose (Appendix 1 and 2).

There was a wide variation observed in the Zn content of the groundwater. The recorded level of Zn in all sampling points in the dry season varied from 3.85 - 14.41 µg/L and in the wet season ranged from 3.7 – 61.67 µg/L. The averages levels detected were  $7.55 \pm 9.170$  µg/L (dry) and  $7.97 \pm 2.74$  µg/L (wet). Zn concentrations in the springs water, in both seasons (Appendix 3 and 4) complied with prescribed limits of 3000 µg/L for domestic-water use, set by WHO (2011). Spatial distribution of Zn in spring water, within Thulamela, showed high concentration in the northwest part and low values in the northeast to the southern parts in the wet season. The dry season showed that the upper part of Thulamela Municipality had higher concentrations where values gradually increased from the southern to northern parts (Figure 4.27). A high level of Zn in water, exceeding the guideline limit, may have adverse effects on human health, mostly in children as their immune systems are still weak. Symptoms include diarrhea, fever, and nausea (Mutileni, 2021). Results that were obtained by Munyangane et al. (2017) recorded slightly higher levels of Zn (0-73.2 µg/L) at Giyani, Limpopo Province.

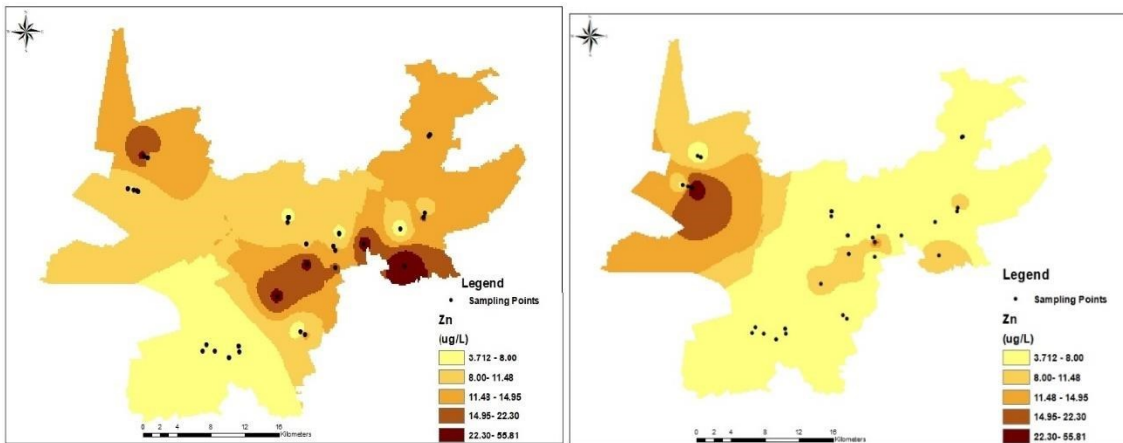


Figure 4.27: Spatial Distribution of Zn (A- wet season and B- dry season)

Mn concentration in the samples varied from 4.06-223.43  $\mu\text{g/L}$  in the dry season while in the wet season the recorded values ranged from 4.623-298.37  $\mu\text{g/L}$ . The mean values recorded in this study were  $25.543 \pm 44.09 \mu\text{g/L}$  (dry) and  $29.4022 \pm 48.697 \mu\text{g/L}$  (Appendix 3 and 4). These detected results fell within the limit for general health  $\leq 400 \mu\text{g/L}$  SANS (2015) and domestic use of  $1000 \mu\text{g/L}$  set by WHO (2011). Manganese is also known to be essential for growth, reproduction and skeletal (cartilage) development, however, it is harmful when consumed in high concentration, causing effects such as skin problems, blood thickening, lowered cholesterol levels, skeleton disorders, birth problems, and neurological manifestations (Saha and Paul, 2019). There was no significant difference between the levels of Mn recorded in the wet and the dry seasons ( $P > 0.05$ ). The spatial map of Mn showed that on the upper part of Thulamela municipality there was high concentration (gradually increased from the southern to northern parts) in the dry season. In the wet season, higher levels were seen in the north eastern part whereas other parts revealed lower levels (Figure 4.28). Edokpayi et al. (2018) recorded lower levels that complied with the SANS (2015) regulatory limit.

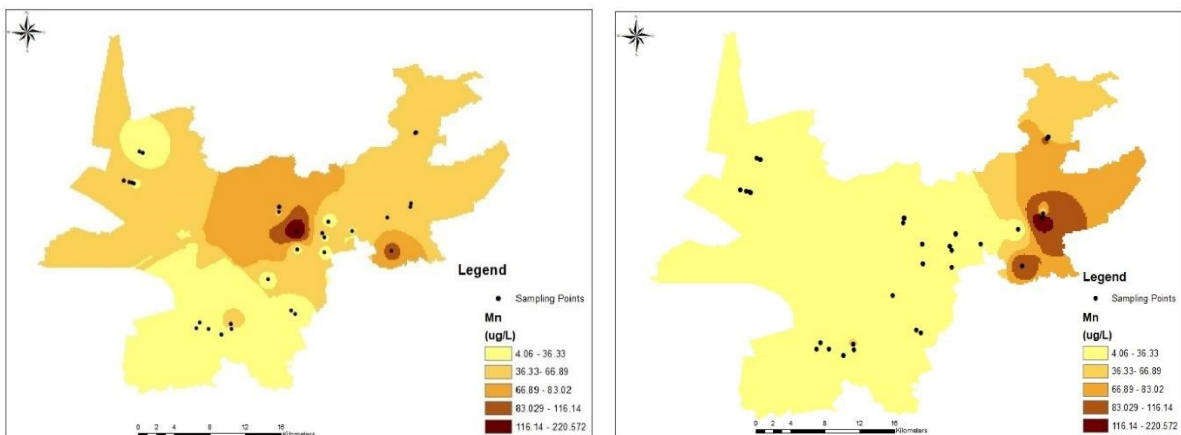


Figure 4.28: Spatial Distribution of Mn (A- wet season and B- dry season)

This study recorded low values of Hg in both seasons but varied between BDL-0.4 µg/L in the dry season and BDL - 0.04 µg/L in the wet season. The averages recorded were  $0.154 \pm 0.1631$  µg/L (dry) and  $0.02 \pm 0.0173$  µg/L (wet) (Appendix 3 and 4). The results fall within the recommended level of  $>1$  µg/L by SANS (2015) and WHO (2011) for domestic use purposes. The water, therefore, is suitable for use in aquaculture, irrigation, recreation, and livestock purposes. The results also indicated that there was no significant difference in the recorded values of Hg for the studied seasons ( $p > 0.05$ ) (Appendix 2).

The concentration of Pb in the studied areas varied from BDL - 8.715 µg/L in the dry season and BDL - 0.995 µg/L in the wet season. The mean levels recorded were  $1.32 \pm 1.8407$  µg/L (dry) and  $0.87 \pm 0.229$  µg/L (wet) (Appendix 3 and 4). The standard guideline of Pb is 10 µg/L (SANS, 2015) and 20 µg/L (WHO, 2011); all of the samples analyzed fell within the limit for domestic, agriculture, and recreation purposes. The results have shown that there was an insignificant difference in the recorded values of Pb for the studied seasons ( $p > 0.05$ ). The presence of Pb can be from manmade and natural sources that leach into the spring water through contact with lead-containing materials like corrosive pipes, leading to ill-health effects on people using the water for domestic purposes (El-Hassanin et al., 2020; Abbasnia et al., 2019). Consumption of water with high levels of Pb can lead to undesirable impacts, like hemoglobin and iron deficiency, kidney harm, miscarriages, fetus removals, and brain harm (Paul et al., 2019). Another study by Durowoju et al. (2020) recorded a range of 0.01- 0.49 µg/L which was lower compared to the results found in this study, however, all of the levels complied with the standard guideline limit.

Iron observed in the water ranged from 152.86 - 1017 µg/L in the dry season and 192.02 - 4533 µg/L in the wet season. The average recorded values were  $364.7 \pm 216.11$  µg/L (dry) and  $576.5 \pm 693.416$  µg/L (wet) (Appendix 3 and 4). The recommended limit for Fe in drinking water is 2000 µg/L. The studied spring water was within the recommended limit of (WHO, 2011 and SANS, 2015) (Appendix 3 and 4). The spatial distribution maps of Fe represented by sampling points in Thulamela Municipality present that the dry season had higher values when compared to the wet season. In the wet season, high concentration was found in the northwest part, while low concentration was determined on the south and north-east sides due to surface runoffs and seeping of water through iron rock bearing. In the dry season, however, the spatial distribution map shows that the values were higher in most parts of the sampling points with the northern side being dominant with higher levels (Figure 4.29). A conducted study by Mudzielwana et al. (2020) revealed lower levels compared to this study and they complied with the standard guideline.

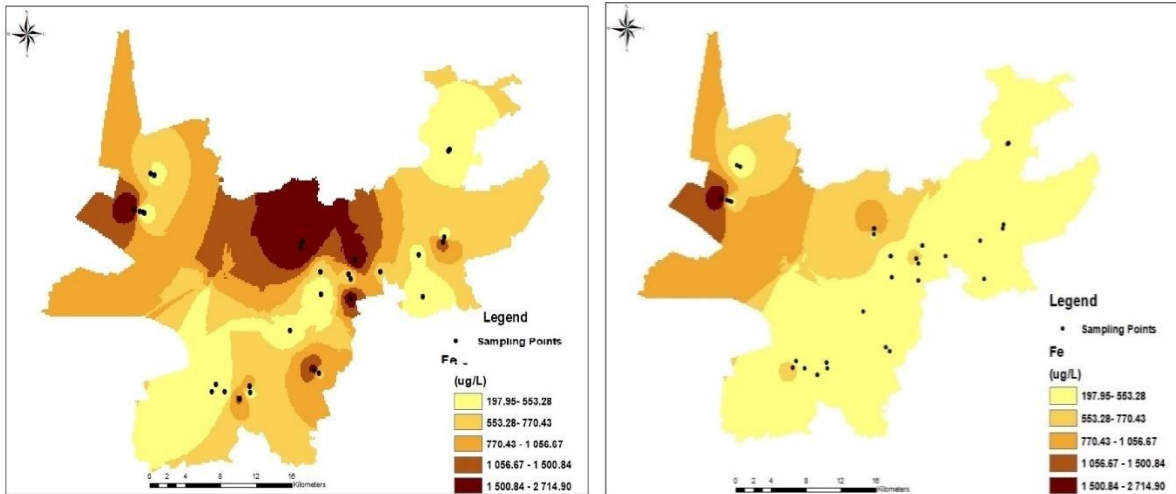


Figure 4.29: Spatial Distribution of Iron (A- dry season and B- wet season)

The concentrations of Co varied from 0.495-1.424  $\mu\text{g/L}$  in the dry season. Furthermore, in the wet season, the levels ranged from 0.59-1.465  $\mu\text{g/L}$ . The averages values computed were  $0.90 \pm 0.37$  (dry) and  $1.06 \pm 0.61$  (wet). The standard limit of Co in drinking water set by SANS (2015) is 5000  $\mu\text{g/L}$  and all of the spring water fell within the standard guideline (Appendix 3 and 4). Concentration values of Co gradually increased from south-east to north-west in the wet season. Figure 4.35 shows the spatial distribution of Co in Thulamela Municipality within the sampling points. In the dry season, Co levels increased from south-west to north-east due to combustion releases and fuel burn. Co is utilised by pregnant women to treat anaemia as it stimulates red blood cells production. The daily intake of Co for a human, however, must not exceed 1 mg as it might have negative effects (Popoola et al., 2019). A study by Luvhimbini et al. (2022) recorded higher levels of Co than what is reported in this study although, they fall within the guideline.

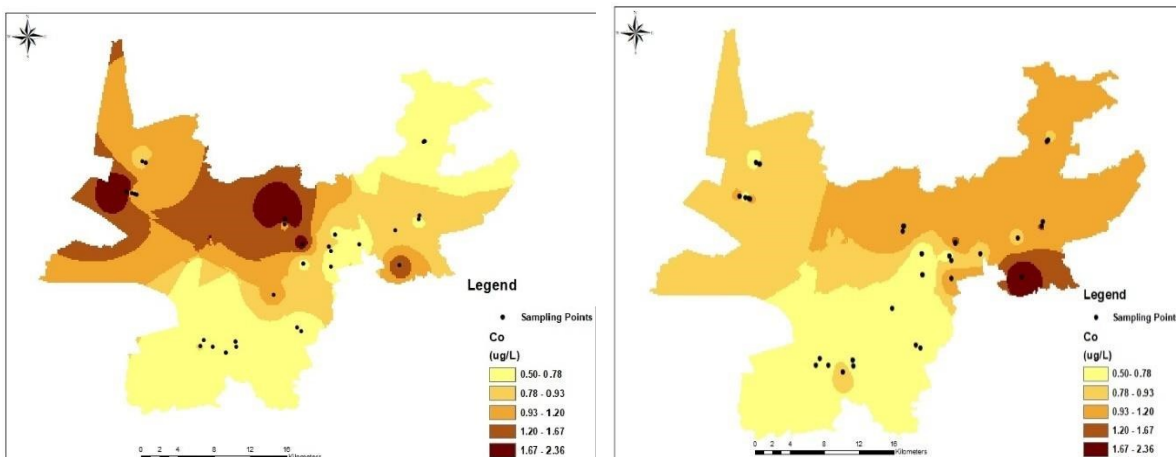


Figure 4.30: Spatial Distribution of Co (A- wet season and B- dry season)

Nickel levels ranged between 9.1-22.475 µg/L in the dry season and 14.78-24.035 µg/L in the wet season. The averages recorded were 17.874±2.465 µg/L (dry) and 20.09±2.962 µg/L (wet). The standard guideline of Ni in drinking water is 70 µg/L and all of the studied spring water complied with the limit set by WHO for drinking water (Appendix 3 and 4), (WHO, 2003). The results represented a significant difference in values of Ni for the studied seasons ( $p < 0.05$ ) with a p-value of 0.004 (Appendix 2). A large intake of Ni may cause dizziness and sickness, heart disorder, asthma, respiratory failure and allergies. The spatial distribution showed a high concentration in the wet season (Figure 4.31), however, the recorded levels of a study done by Mthembu et al. (2022) showed lower Ni levels with a range from BDL- 9.3 µg/L.

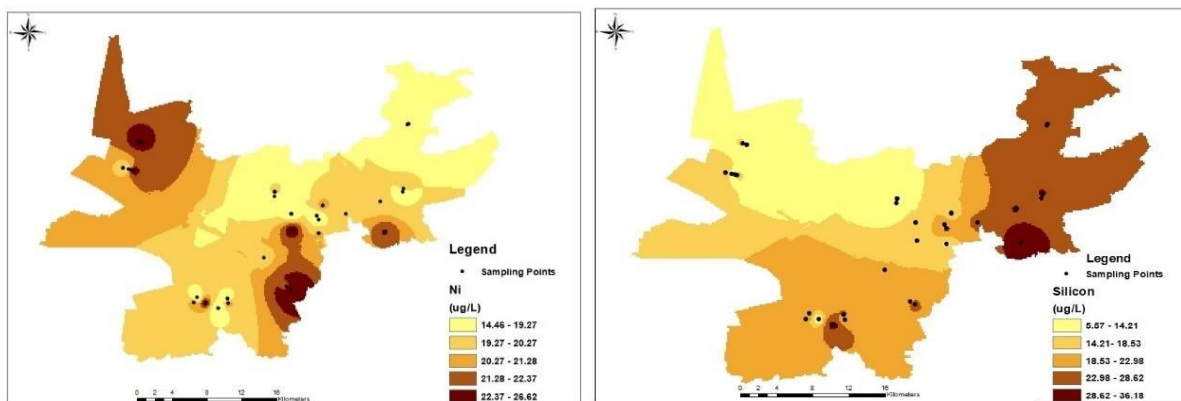


Figure 4.31: Spatial Distribution of Ni (A- wet season and B- dry season)

Cd is determined as one of the high toxic elements to freshwater, for aquatic and marine life; this makes it non-essential. The experimental data on the study area recorded levels of Cd which varied from BDL- 0.075 (dry) and BDL- 0.12 µg/L (wet) with means of 0.065± 0.007 µg/L (dry) and 0.07± 0.0138 µg/L (wet) (Appendix 3 and 4). The levels of Cd for both seasons complied with the WHO standard for the protection of aquatic life ( $1.5 \times 10^{-4}$  µg/L) (WHO, 2011) and SANS for drinking and domestic purposes (3 µg/L) (SANS, 2015). There was no significant difference in the p-value obtained ( $P > 0.05$ ) in the mean level of Cd in dry and wet seasons with a p-value of 0.0616 (Appendix 2). Hazardous waste sites and wastewater from industrials could have influenced the presence of Cd in the springs' water. This can pose a threat to human organs, such as kidney and pulmonary diseases, if ingested. Liu and Ma (2020) showed a range of 0.007-0.016 µg/L for Cd in their study.

The levels of Ba in the dry season varied between 4.88-60.97 µg/L and 6.87-60.8 µg/L in the wet season. The averages recorded were 20.23±17.99 µg/L (dry) and 25.4±20.86µg/L (wet) (Appendix 3 and 4). Ba in spring water is mostly associated with human domestic activities and industries. Small amounts of Ba in the human body may cause increased stomach

irritation, blood pressure, and kidney damage (Pearson, 2020). All the levels of Ba in the studied springs fell within the standard guideline of 700 µg/L of drinking water set by WHO.

The spatial distribution of Ba shows that the values are higher in the southern part and it decreases towards the north in all seasons (Figure 4.32). Comparable results have been recorded by Gao et al. (2020) with 24.39- 67.94 µg/L with Jinzhong spring water samples.

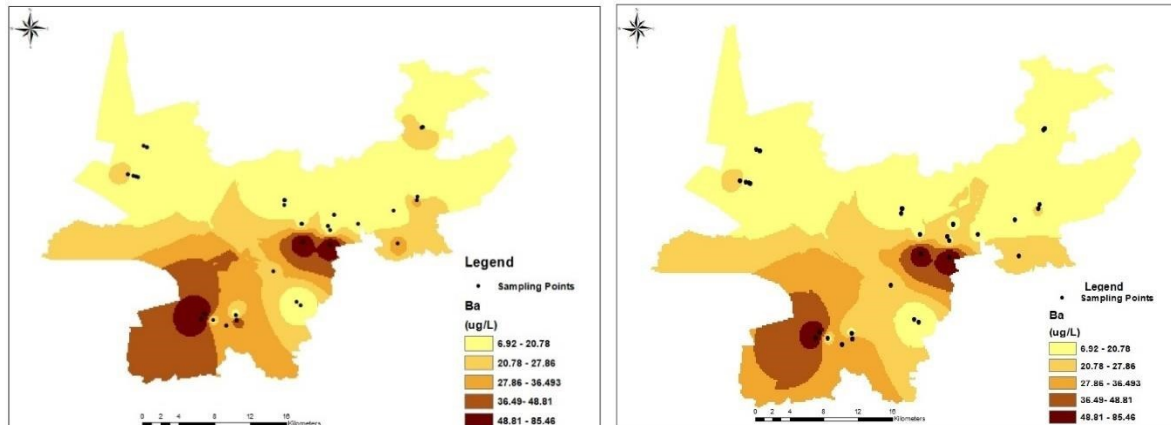


Figure 4.32: Spatial Distribution of Ba (A- wet season and B- dry season)

The recorded values of Cu in the dry season ranged from 2.53-37.12 µg/L and 1.27-25.62 µg/L in the wet season. The averages recorded were  $8.29 \pm 7.96$  µg/L (dry) and  $3.69 \pm 3.86$  µg/L (wet). All of the spring water analyzed, fell within the standard guideline of 2000 µg/L for WHO, for drinking water (Appendix 3 and 4). There was a significant difference in the p-value obtained ( $P < 0.05$ ) in the mean level of Cu for dry and wet seasons (Appendix 2). In the wet season, Figure 4.33 shows lower levels of Cu in the southern part of the study area, whereas in the northern part it gradually increased. In the dry season, however, the concentration increased from the northeast to the southern part. High intake of Cu concentration may cause vomiting, headaches, stomach aches, dizziness, diarrhoea, ill-effects on the lungs and even cause death. The results recorded by Lulambe et al. (2022) showed a lower level of Cu compared to this study.

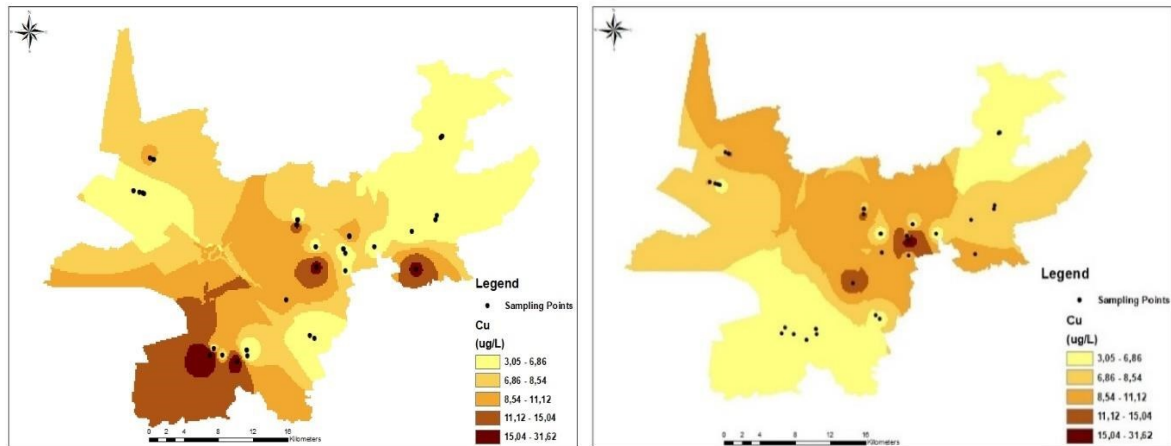


Figure 4.33: Spatial Distribution of Cu (A- wet season and B- dry season)

The levels of Mo in the dry season ranged from 0.495- 1.15  $\mu\text{g/L}$  and 0.6- 1.73  $\mu\text{g/L}$  in the wet season. The averages recorded were  $0.74 \pm 0.15 \mu\text{g/L}$  (dry) and  $0.85 \pm 0.19 \mu\text{g/L}$  (wet). Results from the sampling points were within the threshold of WHO (2011) and SANS (2015) threshold limit (70 mg/L) (Appendix 3 and 4).

The recorded levels of Si differed between 3.23- 29.52  $\mu\text{g/L}$  for the dry season and 5.4336.195 for the wet season; the standard guideline of WHO for drinking water is 5-25 mg/L. In the dry season, almost all of the water samples exceeded the limit, except - S31, S32, S33, S34, S40, and S41. (Appendix 3 and 4). The averages recorded were  $15.73 \pm 7.70 \mu\text{g/L}$  (dry) and  $17.26 \pm 8.12 \mu\text{g/L}$  (wet). Wet season sampled water did not comply with the standard guideline of WHO (2011). Si concentration could be a result of landfill leaching, infiltration, and dumpsite waste (Sohail et al., 2020). The spatial distribution of silicon in the study area was within the standard limit except for the north-east parts for both seasons (figure 4.34). Silicon high level tends to irritate the skin and eyes on contact, while inhalation causes lung cancer (Padmalal et al., 2012).

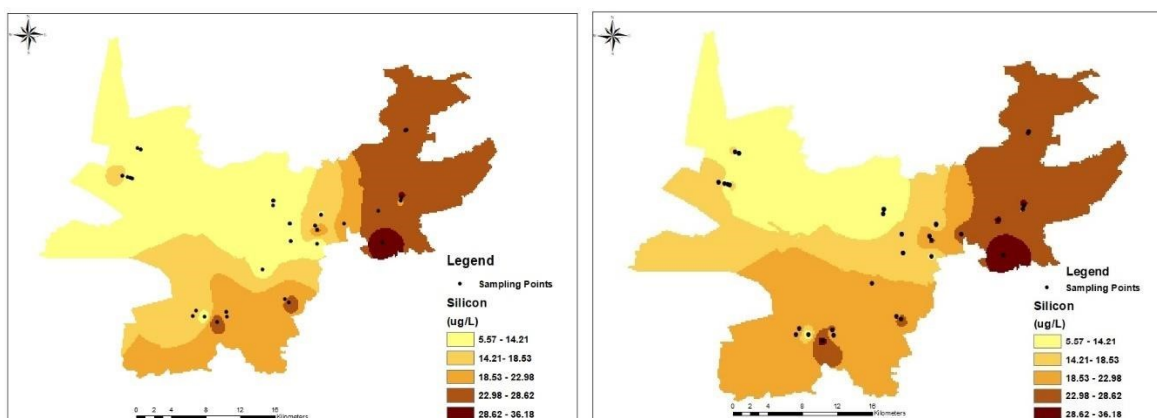


Figure 4.34: Spatial Distribution of Silicon (A- wet season and B- dry season)

The concentration of Al in the spring water samples varied between 400.97-4881  $\mu\text{g/L}$  (dry) and 65.62- 962.745  $\mu\text{g/L}$  (wet); with an average of  $121.527 \pm 105.448$   $\mu\text{g/L}$  (dry) and  $181.77 \pm 163.06$   $\mu\text{g/L}$  (wet); the average of each spring water is presented in (Appendix 3 and 4). The concentration of Al complies with the threshold value by SANS (2015) for domestic water use (1500  $\mu\text{g/L}$ ) and aquatic ecosystem protection (5  $\mu\text{g/L}$ ). Figure (4.35) shows how the values of Al differed in the study area. Furthermore, the parameters revealed a strong correlation in the wet season between Al and Fe at ( $r = 0.96$ ) (Appendix 5 and 6).

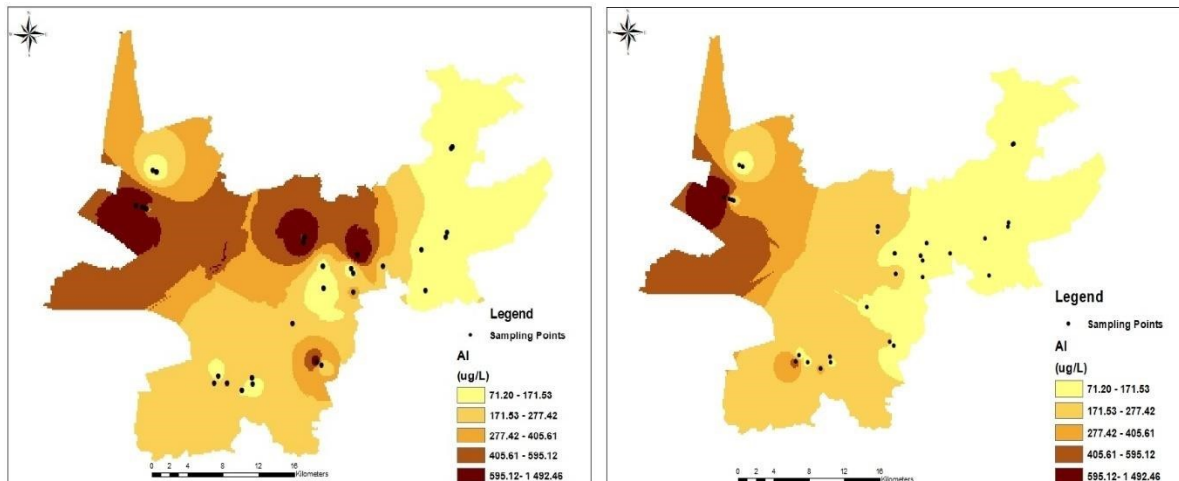


Figure 4.35: Spatial Distribution of Al (A- wet season and B- dry season)

Other parameters that recorded values that complied with the standard guideline of WHO (2011) and SANS (2015) include Vanadium which ranged from 0.5-13.94  $\mu\text{g/L}$  (dry) and 0.435-10.93  $\mu\text{g/L}$  (wet), with an average value of  $2.67 \pm 2.56$   $\mu\text{g/L}$  and  $3.10 \pm 2.93$   $\mu\text{g/L}$  respectively. Sr level showed 5.23-182.66  $\mu\text{g/L}$  (dry) and 9.1-197.57  $\mu\text{g/L}$  (wet). The averages recorded were  $43.98 \pm 40.41$   $\mu\text{g/L}$  (dry) and  $47.09 \pm 41.09$   $\mu\text{g/L}$  (wet). Sn ranged from 13.22-47.32  $\mu\text{g/L}$  (dry) and 53.9-68.48  $\mu\text{g/L}$  (wet) with associated mean values of  $27.76 \pm 6.425$   $\mu\text{g/L}$  and  $60.35 \pm 5.06$   $\mu\text{g/L}$ . Sb revealed levels ranging from 0.03-1.31  $\mu\text{g/L}$  for the dry season and 18.05-104.2  $\mu\text{g/L}$ ; the averages recorded were  $0.17 \pm 0.29$   $\mu\text{g/L}$  (dry) and  $59.34 \pm 29.29$   $\mu\text{g/L}$  (wet). V, Sn, Sb, and Sr recorded values fell within the standard limit of SANS 2015 (<200; n/a; <20; <1500  $\mu\text{g/L}$ ) and WHO, 2011 (15; n/a; 20; 1500  $\mu\text{g/L}$ ) respectively for both dry and wet seasons (Appendix 3 and 4).

The p-value results revealed that some of the trace elements' average levels of the spring water, in both seasons, were not significantly different. The p values recorded were Al (0.121), V (0.4876), Co (0.1487), Se (1,149), Sr (2.1487), Sn (3.1487), Sb (0.992), Fe (0.083), Zn (0,77516), Ba (0.233), (Appendix 2).



#### 4.5 Water Quality Index Analysis (WQI)

The Water Quality Index Analysis was based on all the physicochemical parameters analysed in the study for the dry and wet seasons. Each parameter was assigned with a weight in mg/L based on its effect on spring water quality. The maximum weight of 5 was assigned to a parameter because of its importance in water quality; minimum weight of 1 was assigned to the parameters which were considered insignificant to the overall water quality (Table 4.2). The quality rating scale ( $q_i$ ) was computed for each sampled spring water, as shown in (Table 4.2 and 4.3) using the concentration of each chemical parameter and the desired guideline ( $S_i$ ). The WQI ranks were also recorded to show the status of water quality at each sampling site (Table 4.4 and 4.5).

The computed WQI provided in (Tables 4.4 and 4.5) shows that 100% (dry) and 80.04% (wet) of the sampled spring water can be regarded as having an excellent water quality (water can be used for domestic purposes), whereas 19.51% (wet) can be considered good water quality (it can be utilised for agriculture, although for domestic and recreation only with proper treatment) (Table 4.6). The computed results indicated that WQI ranged from 10.63-50.61 (dry season) and 24.79-86.00 (wet season) with averages and standard deviations of  $20.73 \pm 7.95$  and  $40.94 \pm 15.26$ , respectively (Table 4.4 and 4.5). Furthermore, the spring with excellent water was recorded at S33 (dry) and S41 (wet) and this water is suitable for drinking without treatment as it is not associated with any harm to human health based on the physicochemical parameters used. Good water quality with highest value was detected at S21 (wet) (Table 6).

The computation of WQI traditionally does not include microbial parameters and this is disadvantageous because their presence in water also gives an indication of the quality. If microbial parameters were included in the computation of WQI, most of the water sources will not be considered as having good or excellent water as they need to be treated prior to drinking and other domestic use. Due to the levels of faecal indicator organisms recorded in this study, the overall WQI can be regarded as having minimal quality. The results detected is comparable to the studies conducted by Krishan et al. (2016); Gao et al. (2020); Aydin et al. (2021).

Table 4.2: Quality rating scale (qi) of all the spring water in the dry season

Dry season	Computing qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi	qi				
Parameters	(Wj)	(Wi)	(Si)	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25	S26	S27	S28	S29	S30	S31	S32	S33	S34	S35	S36	S37	S38	S39	S40	S41	
EC (mS/cm)	4	0.0339	≤600.01	23.45	18.77	18.18	18.11	11.41	14.71	14.90	14.70	19.02	21.08	22.18	27.71	34.84	24.00	21.82	33.55	13.65	15.59	18.87	35.48	73.57	44.34	72.41	52.06	18.59	27.81	25.61	14.43	14.70	6.99	5.96	5.79	9.16	18.81	11.13	12.18	41.46	17.49	15.23	7.65	8.29	
Temperature(°C)	2	0.0169	≤25	3.28	89.00	88.87	88.80	89.87	87.60	87.00	89.33	89.07	89.35	91.93	95.13	84.93	84.27	85.93	91.67	89.20	90.80	89.07	90.93	88.13	85.60	87.80	93.60	96.53	94.40	92.28	88.53	86.27	86.07	94.80	86.87	84.20	94.60	93.90	94.27	95.73	93.07	88.73	89.05	92.73	
pH	5	0.0424	6.5-8.5	95.60	99.96	96.58	96.58	96.18	93.09	96.22	93.24	94.20	92.71	95.36	95.51	96.02	97.09	94.91	93.53	97.64	98.40	97.89	99.11	95.87	91.40	90.04	93.73	91.24	95.07	94.36	97.36	98.69	96.76	96.09	97.24	94.09	96.47	93.82	84.62	95.29	94.42	95.96	97.11	96.62	
Salinity (mg/L)	3	0.0254	≤600	11.51	8.32	8.23	8.48	5.37	7.11	7.11	7.39	9.72	9.99	10.59	15.74	19.37	11.89	10.83	17.03	17.36	6.10	8.47	23.70	29.95	20.01	24.47	17.96	8.22	11.64	13.96	7.72	6.73	3.75	3.45	21.05	12.21	18.22	11.78	7.02	17.45	10.41	7.82	5.71	4.13	
TDS (mg/L)	4	0.0339	≤500	18.81	16.13	16.82	16.19	11.67	12.61	13.52	13.41	17.39	18.27	18.97	24.61	30.06	21.43	18.21	28.43	28.86	12.71	17.59	43.81	64.76	46.53	57.04	43.91	15.54	23.84	23.25	12.42	12.56	5.48	5.25	4.31	7.29	16.03	9.46	10.15	33.57	14.20	9.11	6.85	8.19	
Turbidity (NTU)	4	0.0339	≤1	70.67	14.33	21.33	51.67	27.33	98.17	92.17	3.83	0.00	139.83	333.67	207.83	47.17	245.17	232.83	123.67	137.33	167.67	0.00	0.00	3.33	4.83	12.67	27.33	14.67	22.33	9.00	160.00	52.67	524.33	829.33	0.00	3.00	0.00	299.17	382.67	80.33	1097.50	25.50	0.00	145.58	
B (mg/L)	2	0.0169	≤2.4	0.60	0.48	0.36	0.43	0.39	0.36	0.29	0.48	0.31	0.42	0.38	0.70	0.23	0.39	0.41	0.47	0.52	0.25	0.40	0.43	1.80	0.69	0.50	0.70	0.74	0.73	0.41	0.41	0.41	0.42	0.45	0.35	0.31	1.00	0.71	0.73	1.10	0.78	0.85	0.66	0.58	
Al (mg/L)	2	0.0169	≤1.5	6.71	2.42	4.25	4.77	8.44	5.03	6.09	3.33	2.62	7.44	14.51	5.23	5.19	8.07	4.22	3.25	8.55	8.08	3.82	3.31	3.44	4.06	6.08	5.13	5.38	4.91	5.15	32.81	4.89	19.83	26.73	6.49	8.35	4.03	20.83	19.19	4.54	21.30	4.28	5.32	4.10	
V (mg/L)	1	0.0085	≤0.015	14.57	9.00	9.00	10.27	4.80	6.20	7.47	8.60	3.20	10.43	34.90	13.27	10.50	16.10	11.67	27.90	38.17	29.80	13.73	18.27	92.90	18.50	24.77	48.43	13.90	16.57	11.83	26.80	6.20	12.30	22.80	3.33	6.37	6.60	18.93	17.57	58.90	12.57	8.30	3.33	3.63	
Mn (mg/L)	3	0.0254	≤0.4	3.76	2.00	2.00	3.97	3.84	2.92	2.46	2.73	3.46	3.87	2.47	1.84	3.57	3.06	18.30	1.81	2.95	2.14	1.00	43.87	25.91	55.85	4.84	2.72	4.16	4.16	3.21	10.19	1.21	5.27	5.50	6.67	1.82	1.02	2.10	2.98	2.72	2.62	2.36	2.56	1.96	
Fe (mg/L)	3	0.0254	≤2	15.72	13.27	12.97	19.02	27.74	17.23	13.40	10.80	7.64	13.04	25.87	15.33	11.63	15.22	22.31	13.93	28.19	13.69	8.95	12.92	9.09	25.60	10.88	14.23	14.86	15.12	14.89	50.86	9.00	44.61	44.61	14.93	11.66	9.31	11.14	13.15	22.84	47.58	16.61	13.72	14.10	
Co (mg/L)	2	0.0169	≤0.01	8.35	14.25	6.00	7.05	12.30	6.75	6.70	6.80	4.85	6.10	7.95	6.30	7.20	5.95	8.90	8.30	9.25	6.70	5.70	12.70	23.70	13.00	8.85	8.50	8.90	8.85	7.30	20.10	4.95	11.80	10.10	11.20	7.35	12.05	4.95	6.80	10.65	9.75	7.20	8.00	8.10	
Ni (mg/L)	3	0.0254	≤0.07	26.27	26.09	21.65	24.86	30.89	22.66	24.14	32.11	23.00	26.51	27.66	24.19	26.83	19.66	13.00	26.39	28.93	26.98	24.98	23.71	25.07	24.04	27.18	28.02	30.26	25.44	26.34	26.91	21.71	22.94	21.51	27.16	23.61	27.26	20.11	28.20	30.28	30.25	28.42	25.80	25.89	
Cu (mg/L)	2	0.0169	≤2	0.28	0.14	0.15	0.47	0.32	0.32	0.28	1.45	0.22	0.46	0.20	0.15	0.16	0.27	0.13	0.16	1.86	1.61	0.21	0.29	0.82	0.32	0.22	0.24	0.24	0.20	0.38	0.81	0.19	1.02	0.33	0.20	0.21	0.19	0.24	0.39	0.20	0.37	0.49	0.50	0.34	
Zn (mg/L)	2	0.0169	≤5	0.23	0.19	0.20	0.30	0.31	0.23	0.27	0.48	0.26	0.37	0.16	0.28	0.16	0.19	0.24	0.13	0.20	0.17	0.17	0.25	0.46	0.32	0.21	0.18	0.26	0.22	0.38	0.22	0.17	0.22	0.21	0.23	0.17	0.22	0.15	0.31	0.21	0.28	0.42	0.23	0.31	
Cr (mg/L)	3	0.0254	≤0.05	76.38	78.39	64.14	69.81	87.35	65.55	69.91	87.10	61.52	76.11	82.00	67.85	68.92	52.73	37.99	78.24	81.83	87.35	72.96	67.25	60.34	67.41	76.95	77.37	89.59	85.36	73.50	78.16	61.86	69.71	67.92	72.51	67.31	72.73	58.36	79.54	90.79	84.12	75.60	74.48	74.13	
As (mg/L)	5	0.0424	≤0.01	0.70	0.85	0.70	0.70	0.70	BDL	0.70	0.60	0.75	0.85	1.15	0.70	1.00	0.70	0.75	1.20	1.35	1.15	1.20	0.80	1.35	0.95	0.47	0.60	0.85	0.60	0.90	0.90	BDL	BDL	1.05	BDL	BDL	BDL	BDL	BDL	BDL	3.00	1.25	BDL	1.30	0.75
Se (mg/L)	2	0.0169	≤0.04	78.88	62.75	61.60	64.65	133.10	41.80	45.85	76.33	113.60	78.25	87.85	134.45	163.95	84.10	112.65	336.73	360.35	276.23	179.00	165.28	447.73	209.38	215.83	130.25	57.13	87.55	78.70	45.70	50.78	25.33	13.65	14.08	13.90	72.28	28.40	28.40	110.23	56.75	35.58	21.93	23.15	
Sr (mg/L)	2	0.0169	≤1.5	2.37	1.68	1.71	1.74	3.78	1.16	1.23	2.67	2.61	2.04	2.35	3.58	4.44	2.34	2.66	8.81	10.27	7.41	4.94	4.45	12.18	5.61	5.84	3.54	1.68	2.31	1.73	1.29	1.38	0.55	0.46	0.35	0.67	1.77	0.76	0.76	2.99	1.51	1.47	0.59	0.59	
Mo (mg/L)	2	0.0169	≤0.07	1.06	1.14	0.90	0.96	1.09	0.89	0.91	1.37	0.85	1.06	1.09	0.93	1.03	0.71	1.09	1.34	1.51	1.16	1.08	1.01	1.84	0.99	1.11	1.16	1.21	1.11	1.00	0.73	0.86	0.83	0.91	0.95	0.89	1.01	0.78	1.12	1.59	1.23	1.10	1.00	1.03	
Cd (mg/L)	5	0.0424	≤0.003	2.17	2.33	BDL	2.33	2.17	BDL	2.00	2.33	2.00	BDL	BDL	2.33	2.00	BDL	BDL	1.23	2.17	2.33	2.33	BDL	BDL	BDL	2.00	2.67	2.50	2.33	BDL	BDL	BDL	BDL	2.33	2.00	BDL	2.33	BDL	2.17	2.33	2.00	2.00	2.00		
Sn (mg/L)	2	0.0169	n/a	5.74	8.06	12.61	9.15	10.40	10.76	10.87	8.88	9.71	9.90	4.41	9.70	10.95	6.81	8.30	6.22	10.03	9.09	4.91	5.98	6.54	11.12	9.99	9.17	10.06	10.69	9.95	8.33	8.14	10.41	12.74	8.45	8.74	8.99	9.67	8.09	10.33	9.55	15.79	9.65	10.60	
Sb (mg/L)	1	0.0085	≤0.02	2.40	0.23	0.20	0.18	0.28	0.66	0.23	0.25	0.18	4.43	0.30	0.18	6.55	0.23	3.95	0.23	0.18	2.93	3.28	3.50	0.35	0.20	0.23	0.25	0.20	0.63	0.15	0.18	0.25	0.38	0.23	0.20	0.35	0.15	0.18	0.18	0.13	0.70	0.15	0.13		
Ba (mg/L)	3	0.0254	≤0.7	1.59	2.45	2.45	2.33	11.89	1.82	1.88	7.81	8.22	2.34	0.70	1.53	5.63	1.40	1.79	3.76	4.87	8.71	7.96	2.07	3.45	3.10	0.83	0.92	1.57	2.23	1.81	2.07	2.11	1.30	1.29	1.06	1.34	1.99	1.11	1.05	4.49	1.99	1.51	1.07	1.03	
Hg (mg/L)	5	0.0424	≤0.06	0.67	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	1.50	BDL	BDL	3.83	BDL	6.67	BDL	BDL	6.67																							





pH	5	0.0424	6.5-8.5	4.05	4.24	4.09	4.09	4.08	3.94	4.08	3.95	3.99	3.93	4.04	4.05	4.07	4.11	4.02	3.96	4.14	4.17	4.15	4.20	4.06	3.87	3.82	3.97	3.87	4.03	4.00	4.13	4.18	4.10	4.07	4.12	3.99	4.09	3.98	3.59	4.04	4.00	4.07	4.11	4.09		
Salinity (mg/L)	3	0.0254	≤600	0.29	0.21	0.21	0.22	0.14	0.18	0.18	0.19	0.25	0.25	0.27	0.40	0.49	0.30	0.28	0.43	0.44	0.16	0.2	0.60	0.76	0.51	0.62	0.46	0.21	0.30	0.35	0.20	0.17	0.10	0.09	0.54	0.31	0.46	0.30	0.18	0.44	0.26	0.20	0.15	0.10		
TDS (mg/L)	4	0.0339	≤500	0.64	0.55	0.57	0.55	0.40	0.43	0.46	0.45	0.59	0.62	0.64	0.83	1.02	0.73	0.62	0.96	0.98	0.43	0.6	1.48	2.20	1.58	1.93	1.49	0.53	0.81	0.79	0.42	0.43	0.19	0.18	0.15	0.25	0.54	0.32	0.34	1.14	0.48	0.31	0.23	0.28		
Turbidity (NTU)	4	0.0339	≤1	2.40	0.49	0.72	1.75	0.93	3.33	3.12	0.13	0.00	4.74	11.31	7.05	1.60	8.31	7.89	4.19	4.66	5.68	0.0	0.00	0.11	0.16	0.43	0.93	0.50	0.76	0.31	5.42	1.79	17.77	28.11	0.00	0.10	0.00	10.14	12.97	2.72	37.20	0.86	0.00	4.94		
B (mg/L)	2	0.0169	≤2.4	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01		
Al (mg/L)	2	0.0169	≤1.5	0.11	0.04	0.07	0.08	0.14	0.09	0.10	0.06	0.04	0.13	0.25	0.09	0.09	0.14	0.07	0.06	0.14	0.14	0.06	0.06	0.07	0.10	0.09	0.09	0.08	0.09	0.56	0.08	0.34	0.45	0.11	0.14	0.07	0.35	0.33	0.08	0.36	0.07	0.09	0.07			
V (mg/L)	1	0.0085	≤0.015	0.12	0.08	0.08	0.09	0.04	0.05	0.06	0.07	0.03	0.09	0.30	0.11	0.09	0.14	0.10	0.24	0.32	0.25	0.1	0.15	0.79	0.16	0.21	0.41	0.12	0.14	0.10	0.23	0.05	0.10	0.19	0.03	0.05	0.06	0.16	0.15	0.50	0.11	0.07	0.03	0.03		
Mn (mg/L)	3	0.0254	≤0.4	0.10	0.05	0.05	0.10	0.10	0.07	0.06	0.07	0.09	0.10	0.06	0.05	0.09	0.08	0.47	0.05	0.07	0.05	0.0	1.12	0.66	1.42	0.12	0.07	0.11	0.11	0.08	0.26	0.03	0.13	0.14	0.17	0.05	0.03	0.05	0.08	0.07	0.07	0.06	0.07	0.05		
Fe (mg/L)	3	0.0254	≤2	0.40	0.34	0.33	0.48	0.71	0.44	0.34	0.27	0.19	0.33	0.66	0.39	0.30	0.39	0.57	0.35	0.72	0.35	0.23	0.33	0.23	0.65	0.28	0.36	0.38	0.38	0.38	1.29	0.23	1.13	1.13	0.38	0.30	0.24	0.28	0.33	0.58	1.21	0.42	0.35	0.36		
Co (mg/L)	2	0.0169	≤0.01	0.14	0.24	0.10	0.12	0.21	0.11	0.11	0.12	0.08	0.10	0.13	0.11	0.12	0.10	0.15	0.14	0.16	0.11	0.1	0.22	0.40	0.22	0.15	0.14	0.15	0.15	0.12	0.34	0.08	0.20	0.17	0.19	0.12	0.20	0.08	0.12	0.18	0.17	0.12	0.14	0.14		
Ni (mg/L)	3	0.0254	≤0.07	0.67	0.66	0.55	0.63	0.79	0.58	0.61	0.82	0.58	0.67	0.70	0.62	0.68	0.50	0.33	0.67	0.74	0.69	0.6	0.60	0.64	0.61	0.69	0.71	0.77	0.65	0.67	0.68	0.55	0.58	0.55	0.69	0.60	0.69	0.51	0.72	0.77	0.77	0.72	0.66	0.66		
Cu (mg/L)	2	0.0169	≤2	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.03	0.0	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.01	
Zn (mg/L)	2	0.0169	≤5	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.00
Cr (mg/L)	3	0.0254	≤0.05	1.94	1.99	1.63	1.77	2.22	1.67	1.78	2.21	1.56	1.94	2.08	1.73	1.75	1.34	0.97	1.99	2.08	2.22	1.8	1.71	1.53	1.71	1.96	1.97	2.28	2.17	1.87	1.99	1.57	1.77	1.73	1.84	1.71	1.85	1.48	2.02	2.31	2.14	1.92	1.89	1.88		
As (mg/L)	5	0.0424	≤0.01	0.03	0.04	0.03	0.03	BDL	0.03	0.03	0.03	0.04	0.05	0.03	0.04	0.03	0.03	0.05	0.06	0.05	0.0	0.03	0.06	0.04	0.02	0.03	0.04	0.03	0.04	0.04	BDL	BDL	0.04	BDL	BDL	BDL	BDL	BDL	BDL	0.13	0.05	BDL	0.06	0.03		
Se (mg/L)	2	0.0169	≤0.04	1.34	1.06	1.04	1.10	2.26	0.71	0.78	1.29	1.93	1.33	1.49	2.28	2.78	1.43	1.91	5.71	6.11	4.68	3.0	2.80	7.59	3.55	3.66	2.21	0.97	1.48	1.33	0.77	0.86	0.43	0.23	0.24	0.24	1.23	0.48	0.48	1.87	0.96	0.60	0.37	0.39		
Sr (mg/L)	2	0.0169	≤1.5	0.04	0.03	0.03	0.03	0.06	0.02	0.02	0.05	0.04	0.03	0.04	0.06	0.08	0.04	0.05	0.15	0.17	0.13	0.0	0.08	0.21	0.10	0.10	0.06	0.03	0.04	0.03	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.01	0.01	0.05	0.03	0.02	0.01	0.01
Mo (mg/L)	2	0.0169	≤0.07	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.03	0.02	0.0	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.03	0.02	0.02	0.02	0.02	
Cd (mg/L)	5	0.0424	≤0.003	0.09	0.10	BDL	0.10	0.09	BDL	0.08	0.10	0.08	BDL	BDL	0.10	0.08	BDL	BDL	0.05	0.09	0.10	0.1	BDL	BDL	BDL	0.08	0.11	0.11	0.10	BDL	BDL	BDL	BDL	0.10	0.08	BDL	0.10	BDL	0.09	0.10	0.08	0.08	0.08	0.08	0.08	
Sn (mg/L)	2	0.0169	n/a	0.10	0.14	0.21	0.16	0.18	0.18	0.18	0.15	0.16	0.17	0.07	0.16	0.19	0.12	0.14	0.11	0.17	0.15	0.0	0.10	0.11	0.19	0.17	0.16	0.17	0.18	0.17	0.14	0.14	0.18	0.22	0.14	0.15	0.15	0.16	0.14	0.18	0.16	0.27	0.16	0.18		
Sb (mg/L)	1	0.0085	≤0.02	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.06	0.00	0.03	0.00	0.00	0.0	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	
Ba (mg/L)	3	0.0254	≤0.7	0.04	0.06	0.06	0.06	0.30	0.05	0.05	0.20	0.21	0.06	0.02	0.04	0.14	0.04	0.05	0.10	0.12	0.22	0.2	0.05	0.09	0.08	0.02	0.02	0.04	0.06	0.05	0.05	0.05	0.03	0.03	0.03	0.03	0.05	0.03	0.03	0.11	0.05	0.04	0.03	0.03		
Hg (mg/L)	5	0.0424	≤0.06	0.03	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.06	BDL	BDL	0.16	BDL	0.28	BDL	BDL	0.2	0.23	0.20	0.01	BDL	BDL	BDL	BDL	0.01	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.01	BDL	0.01	0.01	BDL	BDL	BDL		
Pb (mg/L)	5	0.0424	≤0.01	0.20	0.17	BDL	0.19	0.20	0.17	0.19	0.18	1.11	0.17	0.23	0.22	BDL	BDL	0.17	0.18	0.82	3.69	0.1	0.19	BDL	0.21	0.22	0.28	0.18	BDL	0.19	0.34	BDL	0.17	0.18	BDL	BDL	0.19	BDL	0.25	0.23	0.22	0.21	2.91	0.17		
Si (mg/L)	2	0.0169	≤0.005-0.025	1.55	0.87	1.10	1.03	0.61	0.74	0.80	0.93	0.77	1.03	1.36	1.41	1.06	1.41	1.40	1.73	2.00	1.16	1.1	1.64	2.23	1.30	1.88	1.75	1.63	1.86	1.21	0.85	0.85	0.33	0.33	0.22	0.33	0.88	0.44	0.42	1.03	0.92	0.97	0.30	0.27		
Mg (mg/L)	2	0.0169	≤150	0.11	0.07	0.08	0.06	0.04	0.04	0.04	0.09	0.07	0.08	0.07	0.16	0.14	0.10	0.10	0.14	0.17	0.05	0.0	0.22	0.48	0.31	0.35	0.21	0.09	0.13	0.10	0.05	0.06	0.02	0.02	0.01	0.02	0.08	0.04	0.04	0.14	0.08	0.10	0.03	0.03		
Na (mg/L)	2	0.0169	≤200	0.07	0.06	0.05	0.05	0.04	0.05	0.05	0.07	0.08	0.07	0.08	0.11	0.11	0.07	0.08	0.12	0.14	0.06	0.0	0.12	0.20	0.16	0.16	0.10	0.06	0.07	0.05	0.05	0.05	0.04	0.03	0.03	0.03	0.05	0.08	0.05	0.04	0.15	0.07	0.08	0.04	0.04	
P (mg/L)	2	0.0169	≤10	0.01	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.03	0.03	0.03	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	
K (mg/L)	2	0.0169	≤20	0.03	0.02	0.02	0.02	0.10	0.02	0.03	0.04	0.04	0.02	0.03	BDL	0.06	0.03	0.05	0.10	0.12	0.15	0.1	0.02	0.03	0.03	0.02	0.03	0.03	0.03	0.05	0.03	0.03	BDL	0.02	BDL	BDL	0.02	BDL	0.02	0.04	0.02	0.13	0.02	0.03		
Ca (mg/L)	2	0.0169	≤200	0.13	0.09	0.10	0.09	0.04	0.05	0.05	0.08	0.06	0.10	0.09	0.18	0.11	0.12	0.15	0.15	0.17	0.05	0.0	0.24	0.43	0.35	0.36	0.25	0.09	0.14	0.10	0.06	0.07	0.02	0.02	0.01	0.02	0.06	0.02	0.02	0.20	0.04	0.07	0.02	0.02		
Br (mg/L)	2	0.0169	≤75	1.63	1.61	BDL	BDL	BDL	BDL	BDL	BDL	1.93	BDL	BDL																																





Table 4.6: Physio-chemical parameters used for WQI determination

	Dry season			Wet season		
<i>Sample ID</i>	<i>WQI</i>	<i>Quality status</i>	<i>Grading</i>	<i>WQI</i>	<i>Quality status</i>	<i>Grading</i>
S1	17.46	Excellent Water	A	31.40	Excellent Water	A
S2	15.65	Excellent Water	A	33.00	Excellent Water	A
S3	13.34	Excellent Water	A	50.45	Excellent Water	A
S4	15.01	Excellent Water	A	35.93	Excellent Water	A
S5	15.71	Excellent Water	A	24.97	Excellent Water	A
S6	15.00	Excellent Water	A	60.14	Good Water	B
S7	15.30	Excellent Water	A	26.17	Excellent Water	A
S8	13.69	Excellent Water	A	32.55	Excellent Water	A
S9	16.24	Excellent Water	A	27.59	Excellent Water	A
S10	18.54	Excellent Water	A	36.91	Excellent Water	A
S11	26.72	Excellent Water	A	50.84	Excellent Water	A
S12	25.91	Excellent Water	A	39.97	Excellent Water	A
S13	18.21	Excellent Water	A	34.96	Excellent Water	A
S14	22.33	Excellent Water	A	38.32	Excellent Water	A
S15	22.14	Excellent Water	A	53.13	Good Water	B
S16	27.64	Excellent Water	A	71.96	Good Water	B
S17	27.33	Excellent Water	A	50.18	Excellent Water	A
S18	26.94	Excellent Water	A	67.59	Good Water	B
S19	16.26	Excellent Water	A	24.31	Excellent Water	A
S20	22.12	Excellent Water	A	30.79	Excellent Water	A
S21	33.53	Excellent Water	A	86.00	Good Water	B
S22	24.16	Excellent Water	A	38.95	Excellent Water	A
S23	26.04	Excellent Water	A	36.38	Excellent Water	A
S24	21.86	Excellent Water	A	34.45	Excellent Water	A
S25	16.82	Excellent Water	A	82.82	Good Water	B
S26	18.13	Excellent Water	A	52.67	Good Water	B



S27	16.63	Excellent Water	A	33.98	Excellent Water	A
S28	20.05	Excellent Water	A	34.76	Excellent Water	A
S29	13.37	Excellent Water	A	27.42	Excellent Water	A
S30	29.44	Excellent Water	A	37.11	Excellent Water	A
S31	39.93	Excellent Water	A	46.81	Excellent Water	A
S32	10.73	Excellent Water	A	33.29	Excellent Water	A
S33	10.36	Excellent Water	A	26.69	Excellent Water	A
S34	15.40	Excellent Water	A	32.89	Excellent Water	A
S35	21.02	Excellent Water	A	33.90	Excellent Water	A
S36	24.53	Excellent Water	A	27.06	Excellent Water	A
S37	22.58	Excellent Water	A	51.74	Good Water	B
S38	50.61	Excellent Water	A	51.02	Excellent Water	A
S39	13.51	Excellent Water	A	32.953	Excellent Water	A
S40	13.66	Excellent Water	A	31.40	Excellent Water	A
S41	15.88	Excellent Water	A	24.78	Excellent Water	A
<i>Average</i>	20.73			40.94		
<i>Min</i>	10.63			24.79		
<i>Max</i>	50.61			86.00		
<i>SD</i>	7.95			15.26		

## 4.6 Health risk assessment

### Carcinogenic and Non- Carcinogenic Risk Analyses

Trace elements in water can increase human health risks, using different exposure routes (Mohammadi et al., 2019). In the current work, non-cancer causing, and cancer-causing risks brought about by dermal and ingestion routes were investigated. Outline of Hazard Quotient (HQ) and Cancer Risk (CR) values for minor components in drinking water through different exposures was measured for children and adults (Tables 4.7 - 4.10).

#### 4.6.1 Non-Carcinogenic risk

Human wellbeing hazard evaluation's purpose is to give assurance of the nature and size of any adversity against the wellbeing of people who may be easily exposed to metals in an environment that is contaminated. In this current study, type of exposure and assessments of hazards were done using the USEPA technique. The trace elements that human beings are exposed to occur through drinking water, eating food, soil, and residue. Human beings' exposure to metals is associated with their daily intake of contaminated substances (USEPA, 1989). Ingestion through drinking water or dermal adsorption was determined in this study.

The elements - Cd, Ba, Fe, Mn, As, Ni, Zn, Pb, Cr, and Cu - were used to evaluate non-carcinogenic human wellbeing hazard related to these metals, in this study. The processes including,  $Exp_{ing}$ ;  $Exp_{der}$ ;  $HQ_{ing}$ ;  $HQ_{der}$  and HI were computed using the observed trace elements per the samples of spring water. The degrees of exposure through dermal and ingestion contact was assessed, since these are the significant exposure pathways of spring water in Thulamela Municipality. The possible wellbeing hazard, related to the exposure through ingestion relies upon the age, weight, and volume of the spring water utilized by an individual (child and adult), as introduced in (Table 4.7-4.10) below.

HQ is used to estimate the harmful potential presented by each component of exposure. According to USEPA (1989) trace elements' toxin can present potential negative effects to human wellbeing when the value of HQ of a metal is more than 1. In the current review, the majority of the HQ values for dermal and ingestion were all lower than 1 (Tables 4.7 - 4.10), therefore, the values found that the studied metals were not capable of negative health risks associated with ingestion or dermal contact for children and adults. 100 % of the HQs values, in both seasons for adults (dermal and ingestion) and children (dermal) fell within the standard guideline ( $HQ < 1$ ) of USEPA (1989).

HQ computed for each trace element was added and expressed as a Hazard Index (HI) (sum of HQs). The HI of the selected trace elements in the sampled springs did not exceed the threshold of 1 for the adults and children via both pathways (Tables 4.7 - 4.10). The recorded results for HI showed very low or no adverse effects, therefore, the studied metals do not have a cumulative potential to cause carcinogenic adverse health effects on both adults and children through direct ingestion and dermal contact with water from Thulamela Municipality. Comparative cases have been investigated which showed non-carcinogenic levels associated with the utilisation of spring water (Rahman et al., 2020; Elemile et al., 2020); Enitan et al., 2018).

**Table 4.7: Human health risk assessment indices for  $Exp_{ing}$ ;  $Exp_{der}$ ;  $HQ_{ing}$ ;  $HQ_{der}$  and  $HI$  of studied metals for the Adult (Dry season)**

Adult dry	Mn				Fe				Ni				Cu				Zn				Cr				As				Mo				Cd				Ba				Pb			
Spring	Ing	Der	HQ Ing	HQ Der	Ing	Der	HQ Ing	HQ Der	Ing	Der	HQ Ing	HQ Der	Ing	Der	HQ Ing	HQ Der	Ing	Der	HQ Ing	HQ Der	Ing	Der	HQ Ing	HQ Der	Ing	Ing	Der	Der	Ing	Der	HQ Ing	HQ Der	Ing	Der	HQ Ing	HQ Der	Ing	Der	HQ Ing	HQ Der	Ing	Der	HQ Ing	HQ Der
S1	4.7E-01	2.2E-03	2.0E-03	1.6E-06	9.9E+00	4.7E-02	1.4E-05	3.4E-07	5.8E-01	5.5E-04	2.9E-04	1.0E-07	1.8E-01	8.4E-04	4.8E-04	3.5E-06	3.7E-01	1.0E-03	1.2E-03	1.6E-06	1.2E+00	1.1E-02	4.0E-04	3.8E-06	2.2E-03	1.0E-05	7.3E-08	3.5E-10	2.3E-02	1.1E-04	4.7E-03	4.4E-03	2.0E-03	9.7E-06	2.0E-06	9.7E-09	3.5E-01	1.7E-03	1.7E-05	8.3E-06	1.5E-02	2.8E-04	4.2E-06	5.3E-09
S2	2.5E-01	1.2E-03	1.0E-03	8.3E-07	8.3E+00	4.0E-02	1.2E-05	2.8E-07	5.7E-01	5.4E-04	2.9E-04	1.0E-07	8.8E-02	4.2E-04	2.4E-04	1.7E-06	1.8E-01	5.0E-04	5.9E-04	7.9E-07	1.2E+00	1.2E-02	4.1E-04	3.9E-06	2.7E-03	1.3E-05	8.9E-08	4.2E-10	2.5E-02	1.2E-04	5.0E-03	4.8E-03	2.2E-03	1.0E-05	2.2E-06	1.0E-08	5.4E-01	2.6E-03	2.6E-05	1.3E-05	1.3E-02	2.4E-04	3.7E-06	4.7E-09
S3	2.5E-01	1.2E-03	1.0E-03	8.3E-07	8.2E+00	3.9E-02	1.2E-05	2.8E-07	4.8E-01	4.5E-04	2.4E-04	8.4E-08	9.2E-02	4.4E-04	2.5E-04	1.8E-06	1.9E-01	5.5E-04	6.4E-04	8.6E-07	1.0E+00	9.6E-03	3.4E-04	3.2E-06	2.2E-03	1.0E-05	7.3E-08	3.5E-10	2.0E-02	9.4E-05	4.0E-03	3.8E-03	BDL	BDL	BDL	BDL	5.4E-01	2.6E-03	2.6E-05	1.3E-05	BDL	BDL	BDL	BDL
S4	5.0E-01	2.4E-03	2.1E-03	1.7E-06	1.2E+01	5.7E-02	1.7E-05	4.1E-07	5.5E-01	5.2E-04	2.7E-04	9.6E-08	2.9E-01	1.4E-03	7.9E-04	5.8E-06	2.9E-01	8.1E-04	9.5E-04	1.3E-06	1.1E+00	1.0E-02	3.7E-04	3.5E-06	2.2E-03	1.0E-05	7.3E-08	3.5E-10	2.1E-02	1.0E-04	4.2E-03	4.0E-03	2.2E-03	1.0E-05	2.2E-06	1.0E-08	5.1E-01	2.4E-03	2.5E-05	1.2E-05	1.4E-02	2.7E-04	4.1E-06	5.2E-09
S5	4.8E-01	2.3E-03	2.0E-03	1.6E-06	1.7E+01	8.3E-02	2.5E-05	5.9E-07	6.8E-01	6.4E-04	3.4E-04	1.2E-07	2.0E-01	9.5E-04	5.4E-04	3.9E-06	2.9E-01	8.2E-04	9.6E-04	1.3E-06	1.4E+00	1.3E-02	4.6E-04	4.3E-06	2.2E-03	1.0E-05	7.3E-08	3.5E-10	2.4E-02	1.1E-04	4.8E-03	4.6E-03	2.0E-03	9.7E-06	2.0E-06	9.7E-09	2.6E+00	1.2E-02	1.3E-04	6.2E-05	1.5E-02	2.8E-04	4.2E-06	5.3E-09
S6	3.7E-01	1.7E-03	1.5E-03	1.2E-06	1.1E+01	5.1E-02	1.5E-05	3.7E-07	5.0E-01	4.7E-04	2.5E-04	8.8E-08	2.0E-01	9.6E-04	5.5E-04	4.0E-06	2.1E-01	6.0E-04	7.1E-04	9.4E-07	1.0E+00	9.8E-03	3.4E-04	3.3E-06	BDL	BDL	BDL	BDL	2.0E-02	9.3E-05	3.9E-03	3.7E-03	BDL	BDL	BDL	BDL	4.0E-01	1.9E-03	2.0E-05	9.5E-06	1.3E-02	2.4E-04	3.6E-06	4.5E-09
S7	3.1E-01	1.5E-03	1.3E-03	1.0E-06	8.4E+00	4.0E-02	1.2E-05	2.9E-07	5.3E-01	5.0E-04	2.7E-04	9.3E-08	1.7E-01	8.2E-04	4.7E-04	3.4E-06	2.6E-01	7.3E-04	8.5E-04	1.1E-06	1.1E+00	1.0E-02	3.7E-04	3.5E-06	2.2E-03	1.0E-05	7.3E-08	3.5E-10	2.0E-02	9.5E-05	4.0E-03	3.8E-03	1.9E-03	8.9E-06	1.9E-06	8.9E-09	4.1E-01	2.0E-03	2.0E-05	9.8E-06	1.4E-02	2.7E-04	4.1E-06	5.2E-09
S8	3.4E-01	1.6E-03	1.4E-03	1.1E-06	6.8E+00	3.2E-02	9.7E-06	2.3E-07	7.1E-01	6.7E-04	3.5E-04	1.2E-07	9.1E-01	4.3E-03	2.5E-03	1.8E-05	4.5E-01	1.3E-03	1.5E-03	2.0E-06	1.4E+00	1.3E-02	4.6E-04	4.3E-06	1.9E-03	8.9E-06	6.3E-08	3.0E-10	3.0E-02	1.4E-04	6.0E-03	5.7E-03	2.2E-03	1.0E-05	2.2E-06	1.0E-08	1.7E+00	8.1E-03	8.4E-05	4.1E-05	1.4E-02	2.6E-04	3.9E-06	4.9E-09
S9	4.4E-01	2.1E-03	1.8E-03	1.4E-06	4.8E+00	2.3E-02	6.9E-06	1.6E-07	5.1E-01	4.8E-04	2.5E-04	8.9E-08	1.4E-01	6.6E-04	3.8E-04	2.7E-06	2.4E-01	6.9E-04	8.1E-04	1.1E-06	9.7E-01	9.2E-03	3.2E-04	3.1E-06	2.4E-03	1.1E-05	7.9E-08	3.7E-10	1.9E-02	8.9E-05	3.7E-03	3.5E-03	1.9E-03	8.9E-06	1.9E-06	8.9E-09	1.8E+00	8.6E-03	8.9E-05	4.3E-05	8.2E-02	1.6E-03	2.4E-05	3.0E-08
S10	4.9E-01	2.3E-03	2.0E-03	1.6E-06	8.2E+00	3.9E-02	1.2E-05	2.8E-07	5.8E-01	5.5E-04	2.9E-04	1.0E-07	2.9E-01	1.4E-03	7.8E-04	5.7E-06	3.5E-01	9.9E-04	1.2E-03	1.5E-06	1.2E+00	1.1E-02	4.0E-04	3.8E-06	2.7E-03	1.3E-05	8.9E-08	4.2E-10	2.3E-02	1.1E-04	4.7E-03	4.4E-03	BDL	BDL	BDL	BDL	5.2E-01	2.4E-03	2.5E-05	1.2E-05	1.3E-02	2.4E-04	3.6E-06	4.5E-09
S11	3.1E-01	1.5E-03	1.3E-03	1.0E-06	1.6E+00	7.7E-02	2.3E-05	5.5E-07	6.1E-01	5.8E-04	3.0E-04	1.1E-07	1.3E-01	6.1E-04	3.5E-04	2.5E-06	1.5E-01	4.3E-04	5.0E-04	6.7E-07	1.3E+00	1.2E-02	4.3E-04	4.1E-06	3.6E-03	1.7E-05	1.2E-07	5.7E-10	2.4E-02	1.1E-04	4.8E-03	4.5E-03	BDL	BDL	BDL	BDL	1.5E-01	7.3E-04	7.5E-06	3.6E-06	1.7E-02	3.2E-04	4.8E-06	6.1E-09
S12	2.3E-01	1.1E-03	9.6E-04	7.7E-07	9.6E+00	4.6E-02	1.4E-05	3.3E-07	5.3E-01	5.1E-04	2.7E-04	9.4E-08	9.6E-02	4.5E-04	2.6E-04	1.9E-06	2.6E-01	7.5E-04	8.8E-04	1.2E-06	1.1E+00	1.0E-02	3.6E-04	3.4E-06	2.2E-03	1.0E-05	7.3E-08	3.5E-10	2.0E-02	9.7E-05	4.1E-03	3.9E-03	2.2E-03	1.0E-05	2.2E-06	1.0E-08	3.4E-01	1.6E-03	1.7E-05	8.0E-06	1.6E-02	3.0E-04	4.6E-06	5.8E-09
S13	4.5E-01	2.1E-03	1.9E-03	1.5E-06	7.3E+00	3.5E-02	1.0E-05	2.5E-07	5.9E-01	5.6E-04	3.0E-04	1.0E-07	9.9E-02	4.7E-04	2.7E-04	2.0E-06	1.5E-01	4.3E-04	5.0E-04	6.6E-07	1.1E+00	1.0E-02	3.6E-04	3.4E-06	3.1E-03	1.5E-05	1.0E-07	5.0E-10	2.3E-02	1.1E-04	4.5E-03	4.3E-03	1.9E-03	8.9E-06	1.9E-06	8.9E-09	1.2E+00	5.9E-03	6.1E-05	2.9E-05	BDL	BDL	BDL	BDL
S14	3.8E-01	1.8E-03	1.6E-03	1.3E-06	9.6E+00	4.5E-02	1.4E-05	3.2E-07	4.3E-01	4.1E-04	2.2E-04	7.6E-08	1.7E-01	8.2E-04	4.7E-04	3.4E-06	1.8E-01	5.1E-04	5.9E-04	7.9E-07	8.3E-01	7.9E-03	2.8E-04	2.6E-06	2.2E-03	1.0E-05	7.3E-08	3.5E-10	1.6E-02	7.4E-05	3.1E-03	3.0E-03	BDL	BDL	BDL	BDL	3.1E-01	1.5E-03	1.5E-05	7.3E-06	BDL	BDL	BDL	BDL
S15	2.3E+00	1.1E-02	9.6E-03	7.6E-06	1.4E+01	6.7E-02	2.0E-05	4.8E-07	2.9E-01	2.7E-04	1.4E-04	5.0E-08	8.0E-02	3.8E-04	2.1E-04	1.6E-06	2.3E-01	6.4E-04	7.5E-04	1.0E-06	6.0E-01	5.7E-03	2.0E-04	1.9E-06	2.4E-03	1.1E-05	7.9E-08	3.7E-10	2.4E-02	1.1E-04	4.8E-03	4.5E-03	BDL	BDL	BDL	BDL	3.9E-01	1.9E-03	1.9E-05	9.3E-06	1.3E-02	2.4E-04	3.7E-06	4.7E-09
S16	2.3E-01	1.1E-03	9.5E-04	7.5E-07	8.8E+00	4.2E-02	1.3E-05	3.0E-07	5.8E-01	5.5E-04	2.9E-04	1.0E-07	1.0E-01	4.8E-04	2.7E-04	2.0E-06	1.2E-01	3.4E-04	4.0E-04	5.4E-07	1.2E+00	1.2E-02	4.1E-04	3.9E-06	3.8E-03	1.8E-05	1.3E-07	6.0E-10	2.9E-02	1.4E-04	5.9E-03	5.6E-03	1.2E-03	5.5E-06	1.2E-06	5.5E-09	8.3E-01	3.9E-03	4.1E-05	2.0E-05	1.4E-02	2.6E-04	3.9E-06	4.9E-09
S17	3.7E-01	1.8E-03	1.5E-03	1.2E-06	1.8E+01	8.4E-02	2.5E-05	6.0E-07	6.4E-01	6.0E-04	3.2E-04	1.1E-07	1.2E+00	5.5E-03	3.2E-03	2.3E-05	1.9E-01	5.4E-04	6.3E-04	8.4E-07	1.3E+00	1.2E-02	4.3E-04	4.1E-06	4.2E-03	2.0E-05	1.4E-07	6.7E-10	3.3E-02	1.6E-04	6.6E-03	6.3E-03	2.0E-03	9.7E-06	2.0E-06	9.7E-09	1.1E+00	5.1E-03	5.2E-05	6.1E-05	1.2E-02	1.7E-04	2.2E-06	2.2E-08
S18	2.7E-01	1.3E-03	1.1E-03	8.9E-07	8.6E+00	4.1E-02	1.2E-05	2.9E-07	5.9E-01	5.6E-04	3.0E-04	1.0E-07	1.0E+00	4.8E-03	2.7E-03	2.0E-05	1.6E-01	4.7E-04	5.5E-04	7.3E-07	1.4E+00	1.3E-02	4.6E-04	4.3E-06	3.6E-03	1.7E-05	1.2E-07	5.7E-10	2.6E-02	1.2E-04	5.1E-03	4.9E-03	2.2E-03	1.0E-05	2.2E-06	1.0E-08	1.9E+00	9.1E-03	9.4E-05	4.5E-05	2.7E-01	5.2E-03	7.8E-05	9.9E-08
S19	1.3E-01	5.9E-04	5.2E-04	4.2E-07	5.6E+00	2.7E-02	8.0E-06	1.9E-07	5.5E-01	5.2E-04	2.7E-04	9.7E-08	1.3E-01	6.2E-04	3.5E-04	2.6E-06	1.6E-01	4.5E-04	5.2E-04	7.0E-07	1.1E+00	1.1E-02	3.8E-04	3.6E-06	3.8E-03	1.8E-05	1.3E-07	6.0E-10	2.4E-02	1.1E-04	4.7E-03	4.5E-03	2.2E-03	1.0E-05	2.2E-06	1.0E-08	1.8E+00	8.3E-03	8.6E-05	4.2E-05	1.4E-02	2.7E-04	4.0E-06	5.1E-09
S20	5.5E+00	2.6E-02	2.3E-02	1.8E-05	8.1E+00	3.9E-02	1.2E-05	2.8E-07	5.2E-01	5.0E-04	2.6E-04	9.2E-08	1.8E-01	8.7E-04	5.0E-04	3.6E-06	2.4E-01	6.8E-04	7.9E-04	1.1E-06	1.1E+00	1.0E-02	3.5E-04	3.3E-06	2.5E-03	1.2E-05	8.4E-08	4.0E-10	2.2E-02	1.1E-04	4.4E-03	4.2E-03	BDL	BDL	BDL	BDL	4.5E-01	2.2E-03	2.2E-05	1.1E-05	1.4E-02	2.7E-04	4.0E-06	5.1E-09
S21	3.3E+00	1.5E-02	1.4E-02	1.1E-05	5.7E+00	2.7E-02	8.2E-06	1.9E-07	5.5E-01	5.2E-04	2.8E-04	9.7E-08	5.1E-01	2.4E-03	1.4E-03	1.0E-05	4.4E-01	1.2E-03	1.5E-03	1.9E-06	9.5E-01	9.0E-03	3.2E-04	3.0E-06	4.2E-03	2.0E-05	1.4E-07	6.7E-10	4.0E-02	1.9E-04	8.1E-03	7.7E-03	BDL	BDL	BDL	BDL	7.6E-01	3.6E-03	3.7E-05	1.8E-05	BDL	BDL	BDL	BDL
S22	7.0E+00	3.3E-02	2.9E-02	2.3E-05	1.6E+01	7.6E-02	2.3E-05	5.5E-07	5.3E-01	5.0E-04	2.6E-04	9.3E-08	2.0E-01	9.6E-04	5.5E-04	4.0E-06	3.0E-01	8.6E-04	1.0E-03	1.3E-06	1.1E+00	1.0E-02	3.5E-04	3.4E-06	3.0E-03	1.4E-05	1.0E-07	4.7E-10	2.2E															

S26	5.2E-01	2.5E-03	2.2E-03	1.7E-06	9.5E+00	4.5E-02	1.4E-05	3.2E-07	5.6E-01	5.3E-04	2.8E-04	9.8E-08	1.2E-01	5.8E-04	3.3E-04	2.4E-06	2.1E-01	6.0E-04	7.1E-04	9.4E-07	1.3E+00	1.3E-02	4.5E-04	4.2E-06	1.9E-03	8.9E-06	6.3E-08	3.0E-10	2.5E-02	1.2E-04	4.9E-03	4.7E-03	2.2E-03	1.0E-05	2.2E-06	1.0E-08	4.9E-01	2.3E-03	2.4E-05	1.2E-05	BDL	BDL	BDL	BDL
S27	4.0E-01	1.9E-03	1.7E-03	1.3E-06	9.4E+00	4.4E-02	1.3E-05	3.2E-07	5.8E-01	5.5E-04	2.9E-04	1.0E-07	2.4E-01	1.1E-03	6.5E-04	4.7E-06	3.6E-01	1.0E-03	1.2E-03	1.6E-06	1.2E+00	1.1E-02	3.9E-04	3.7E-06	2.8E-03	1.3E-05	9.4E-08	4.5E-10	2.2E-02	1.0E-04	4.4E-03	4.2E-03	BDL	BDL	BDL	BDL	4.0E-01	1.9E-03	2.0E-05	9.4E-06	1.4E-02	2.6E-04	4.0E-06	5.0E-09
S28	1.3E+00	6.1E-03	5.3E-03	4.3E-06	3.2E+01	1.5E-01	4.6E-05	1.1E-06	5.9E-01	5.6E-04	3.0E-04	1.0E-07	5.1E-01	2.4E-03	1.4E-03	1.0E-05	2.1E-01	6.0E-04	7.0E-04	9.3E-07	1.2E+00	1.2E-02	4.1E-04	3.9E-06	2.8E-03	1.3E-05	9.4E-08	4.5E-10	1.6E-02	7.6E-05	3.2E-03	3.0E-03	BDL	BDL	BDL	BDL	4.6E-01	2.2E-03	2.2E-05	1.1E-05	2.5E-02	4.8E-04	7.3E-06	9.2E-09
S29	1.5E-01	7.2E-04	6.4E-04	5.1E-07	5.7E+00	2.7E-02	8.1E-06	1.9E-07	4.8E-01	4.5E-04	2.4E-04	8.4E-08	1.2E-01	5.6E-04	3.2E-04	2.3E-06	1.6E-01	4.4E-04	5.2E-04	6.9E-07	9.7E-01	9.2E-03	3.2E-04	3.1E-06	BDL	BDL	BDL	BDL	1.9E-02	8.9E-05	3.8E-03	3.6E-03	BDL	BDL	BDL	BDL	4.6E-01	2.2E-03	2.3E-05	1.1E-05	BDL	BDL	BDL	BDL
S30	6.6E-01	3.1E-03	2.8E-03	2.2E-06	2.8E+01	1.3E-01	4.0E-05	9.5E-07	5.0E-01	4.8E-04	2.5E-04	8.9E-08	6.4E-01	3.0E-03	1.7E-03	1.3E-05	2.0E-01	5.8E-04	6.8E-04	9.0E-07	1.1E+00	1.0E-02	3.7E-04	3.5E-06	BDL	BDL	BDL	BDL	1.8E-02	8.7E-05	3.6E-03	3.5E-03	BDL	BDL	BDL	BDL	2.9E-01	1.4E-03	1.4E-05	6.8E-06	1.3E-02	2.4E-04	3.7E-06	4.7E-09
S31	6.9E-01	3.3E-03	2.9E-03	2.3E-06	2.8E+01	1.3E-01	4.0E-05	9.5E-07	4.7E-01	4.5E-04	2.4E-04	8.3E-08	2.0E-01	9.7E-04	5.5E-04	4.1E-06	2.0E-01	5.7E-04	6.7E-04	8.9E-07	1.1E+00	1.0E-02	3.6E-04	3.4E-06	3.3E-03	1.6E-05	1.1E-07	5.2E-10	2.0E-02	9.5E-05	4.0E-03	3.8E-03	2.2E-03	1.0E-05	2.2E-06	1.0E-08	2.8E-01	1.3E-03	1.4E-05	6.7E-06	1.3E-02	2.5E-04	3.8E-06	4.8E-09
S32	8.4E-01	4.0E-03	3.5E-03	2.8E-06	9.4E+00	4.5E-02	1.3E-05	3.2E-07	6.0E-01	5.7E-04	3.0E-04	1.1E-07	1.3E-01	6.0E-04	3.4E-04	2.5E-06	2.2E-01	6.2E-04	7.2E-04	9.6E-07	1.1E+00	1.1E-02	3.8E-04	3.6E-06	BDL	BDL	BDL	BDL	2.1E-02	9.9E-05	4.2E-03	4.0E-03	1.9E-03	8.9E-06	1.9E-06	8.9E-09	2.3E-01	1.1E-03	1.1E-05	5.5E-06	BDL	BDL	BDL	BDL
S33	2.3E-01	1.1E-03	9.5E-04	7.6E-07	7.3E+00	3.5E-02	1.0E-05	2.5E-07	5.2E-01	4.9E-04	2.6E-04	9.1E-08	1.3E-01	6.4E-04	3.6E-04	2.7E-06	1.6E-01	4.5E-04	5.3E-04	7.0E-07	1.1E+00	1.0E-02	3.5E-04	3.3E-06	BDL	BDL	BDL	BDL	2.0E-02	9.3E-05	3.9E-03	3.7E-03	BDL	BDL	BDL	BDL	2.9E-01	1.4E-03	1.4E-05	7.0E-06	BDL	BDL	BDL	BDL
S34	1.3E-01	6.1E-04	5.3E-04	4.2E-07	5.9E+00	2.8E-02	8.4E-06	2.0E-07	6.0E-01	5.7E-04	3.0E-04	1.1E-07	1.2E-01	5.7E-04	3.2E-04	2.4E-06	2.0E-01	5.8E-04	6.8E-04	9.0E-07	1.1E+00	1.1E-02	3.8E-04	3.6E-06	BDL	BDL	BDL	BDL	2.2E-02	1.1E-04	4.4E-03	4.2E-03	2.2E-03	1.0E-05	2.2E-06	1.0E-08	4.4E-01	2.1E-03	2.1E-05	1.0E-05	1.4E-02	2.6E-04	4.0E-06	5.0E-09
S35	2.6E-01	1.3E-03	1.1E-03	8.8E-07	7.0E+00	3.3E-02	1.0E-05	2.4E-07	4.4E-01	4.2E-04	2.2E-04	7.8E-08	1.5E-01	7.2E-04	4.1E-04	3.0E-06	1.4E-01	3.9E-04	4.6E-04	6.1E-07	9.2E-01	8.7E-03	3.1E-04	2.9E-06	BDL	BDL	BDL	BDL	1.7E-02	8.1E-05	3.4E-03	3.3E-03	BDL	BDL	BDL	BDL	2.4E-01	1.2E-03	1.2E-05	5.8E-06	BDL	BDL	BDL	BDL
S36	3.7E-01	1.8E-03	1.6E-03	1.2E-06	8.3E+00	3.9E-02	1.2E-05	2.8E-07	6.2E-01	5.9E-04	3.1E-04	1.1E-07	2.4E-01	1.1E-03	6.5E-04	4.8E-06	3.0E-01	8.5E-04	9.9E-04	1.3E-06	1.2E+00	1.2E-02	4.2E-04	4.0E-06	BDL	BDL	BDL	BDL	2.5E-02	1.2E-04	4.9E-03	4.7E-03	2.0E-03	9.7E-06	2.0E-06	9.7E-09	2.3E-01	1.1E-03	1.1E-05	5.5E-06	1.9E-02	3.6E-04	5.4E-06	6.8E-09
S37	3.4E-01	1.6E-03	1.4E-03	1.1E-06	1.4E+01	6.8E-02	2.1E-05	4.9E-07	6.7E-01	6.3E-04	3.3E-04	1.2E-07	1.2E-01	5.9E-04	3.3E-04	2.4E-06	2.0E-01	5.6E-04	6.5E-04	8.7E-07	1.4E+00	1.4E-02	4.8E-04	4.5E-06	9.4E-03	4.5E-05	3.1E-07	1.5E-09	3.5E-02	1.7E-04	7.0E-03	6.7E-03	2.2E-03	1.0E-05	2.2E-06	1.0E-08	9.9E-01	4.7E-03	4.8E-05	2.3E-05	1.7E-02	3.2E-04	4.8E-06	6.1E-09
S38	3.3E-01	1.6E-03	1.4E-03	1.1E-06	3.0E+01	1.4E-01	4.3E-05	1.0E-06	6.7E-01	6.3E-04	3.3E-04	1.2E-07	2.3E-01	1.1E-03	6.3E-04	4.6E-06	2.6E-01	7.5E-04	8.8E-04	1.2E-06	1.3E+00	1.3E-02	4.4E-04	4.2E-06	3.9E-03	1.9E-05	1.3E-07	6.2E-10	2.7E-02	1.3E-04	5.4E-03	5.1E-03	1.9E-03	8.9E-06	1.9E-06	8.9E-09	4.4E-01	2.1E-03	2.2E-05	1.0E-05	1.7E-02	3.2E-04	4.8E-06	6.0E-09
S39	3.0E-01	1.4E-03	1.2E-03	9.9E-07	1.0E+01	5.0E-02	1.5E-05	3.5E-07	6.3E-01	5.9E-04	3.1E-04	1.1E-07	3.1E-01	1.5E-03	8.3E-04	6.1E-06	4.0E-01	1.1E-03	1.3E-03	1.8E-06	1.2E+00	1.1E-02	4.0E-04	3.8E-06	BDL	BDL	BDL	BDL	2.4E-02	1.1E-04	4.8E-03	4.6E-03	1.9E-03	8.9E-06	1.9E-06	8.9E-09	3.3E-01	1.6E-03	1.6E-05	7.9E-06	1.5E-02	2.9E-04	4.4E-06	5.6E-09
S40	3.2E-01	1.5E-03	1.3E-03	1.1E-06	8.6E+00	4.1E-02	1.2E-05	2.9E-07	5.7E-01	5.4E-04	2.8E-04	1.0E-07	3.2E-01	1.5E-03	8.5E-04	6.2E-06	2.1E-01	6.0E-04	7.1E-04	9.4E-07	1.2E+00	1.1E-02	3.9E-04	3.7E-06	4.1E-03	1.9E-05	1.4E-07	6.5E-10	2.2E-02	1.0E-04	4.4E-03	4.2E-03	1.9E-03	8.9E-06	1.9E-06	8.9E-09	2.3E-01	1.1E-03	1.1E-05	5.6E-06	2.2E-01	4.1E-03	6.2E-05	7.8E-08
S41	2.5E-01	1.2E-03	1.0E-03	8.2E-07	8.9E+00	4.2E-02	1.3E-05	3.0E-07	5.7E-01	5.4E-04	2.8E-04	1.0E-07	2.1E-01	1.0E-03	5.8E-04	4.2E-06	2.9E-01	8.4E-04	9.8E-04	1.3E-06	1.2E+00	1.1E-02	3.9E-04	3.7E-06	2.4E-03	1.1E-05	7.9E-08	3.7E-10	2.3E-02	1.1E-04	4.5E-03	4.3E-03	1.9E-03	8.9E-06	1.9E-06	8.9E-09	2.3E-01	1.1E-03	1.1E-05	5.4E-06	1.3E-02	2.4E-04	3.6E-06	4.5E-09
HI			<b>1.4E-01</b>	<b>1.1E-04</b>			<b>6.7E-04</b>	<b>1.6E-05</b>			<b>1.2E-02</b>	<b>4.0E-06</b>			<b>2.9E-02</b>	<b>2.1E-04</b>			<b>3.2E-02</b>	<b>4.3E-05</b>			<b>1.6E-02</b>	<b>1.5E-04</b>			<b>3.2E-06</b>	<b>1.5E-08</b>			<b>1.9E-01</b>	<b>1.8E-01</b>			<b>5.3E-05</b>	<b>2.5E-07</b>			<b>1.3E-03</b>	<b>6.2E-04</b>			<b>3.0E-04</b>	<b>3.8E-07</b>



S26	4.04E-01	1.92E-03	1.68E-03	1.34E-06	7.76E+00	3.68E-02	1.11E-05	2.63E-07	6.20E-01	5.88E-04	3.10E-04	1.09E-07	5.11E-02	2.42E-04	1.38E-04	1.01E-06	1.23E-01	3.51E-04	4.11E-04	5.48E-07	1.33E+00	1.26E-02	4.42E-04	4.20E-06	2.20E-03	1.04E-05	7.33E-08	3.48E-10	2.59E-02	1.23E-04	5.19E-03	4.92E-03	2.83E-03	1.34E-05	2.83E-06	1.34E-08	5.02E-01	2.38E-03	2.46E-05	1.19E-05	1.26E-02	2.39E-04	3.59E-06	4.55E-09
S27	5.14E-01	2.44E-03	2.14E-03	1.71E-06	1.02E+01	4.83E-02	1.45E-05	3.45E-07	6.31E-01	5.99E-04	3.15E-04	1.11E-07	8.05E-02	3.82E-04	2.17E-04	1.59E-06	2.08E-01	5.92E-04	6.93E-04	9.24E-07	1.34E+00	1.27E-02	4.46E-04	4.23E-06	3.30E-03	1.57E-05	1.10E-07	5.22E-10	2.62E-02	1.25E-04	5.25E-03	4.98E-03	2.51E-03	1.19E-05	2.51E-06	1.19E-08	5.49E-01	2.60E-03	2.69E-05	1.30E-05	1.29E-02	2.45E-04	3.68E-06	4.66E-09
S28	3.30E-01	1.57E-03	1.38E-03	1.10E-06	1.15E+01	5.45E-02	1.64E-05	3.89E-07	5.75E-01	5.46E-04	2.88E-04	1.01E-07	5.85E-02	2.77E-04	1.58E-04	1.16E-06	1.38E-01	3.93E-04	4.60E-04	6.13E-07	1.22E+00	1.16E-02	4.07E-04	3.86E-06	3.14E-03	1.49E-05	1.05E-07	4.97E-10	2.28E-02	1.08E-04	4.56E-03	4.33E-03	2.04E-03	9.69E-06	2.04E-06	9.69E-09	4.95E-01	2.35E-03	2.43E-05	1.17E-05	BDL	BDL	BDL	BDL
S29	3.99E-01	1.89E-03	1.66E-03	1.32E-06	1.22E+01	5.79E-02	1.74E-05	4.13E-07	7.25E-01	6.88E-04	3.63E-04	1.27E-07	9.24E-02	4.38E-04	2.50E-04	1.83E-06	2.71E-01	7.73E-04	9.05E-04	1.21E-07	1.54E+00	1.46E-02	5.12E-04	4.86E-06	2.51E-03	1.19E-05	8.38E-08	3.98E-10	3.03E-02	1.44E-04	6.07E-03	5.76E-03	2.20E-03	1.04E-05	2.20E-06	1.04E-08	3.52E-01	1.67E-03	1.72E-05	8.35E-06	1.57E-02	2.98E-04	4.49E-06	5.68E-09
S30	4.64E-01	2.20E-03	1.93E-03	1.54E-06	7.48E+00	3.55E-02	1.07E-05	2.54E-07	4.53E-01	4.30E-04	2.27E-04	7.97E-08	2.41E-01	1.14E-03	6.52E-04	4.77E-06	2.29E-01	6.51E-04	7.63E-04	1.02E-07	9.82E-01	9.32E-03	3.27E-04	3.11E-06	2.10E-03	9.94E-06	6.98E-08	3.31E-10	1.89E-02	8.95E-05	3.77E-03	3.58E-03	2.20E-03	1.04E-05	2.20E-06	1.04E-08	4.43E-01	2.10E-03	2.17E-05	1.05E-05	1.32E-02	2.51E-04	3.77E-06	4.77E-09
S31	6.26E-01	2.97E-03	2.61E-03	2.08E-06	1.91E+01	9.08E-02	2.73E-05	6.49E-07	6.16E-01	5.84E-04	3.08E-04	1.08E-07	1.04E-01	4.94E-04	2.82E-04	2.06E-06	1.98E-01	5.64E-04	6.60E-04	8.80E-07	1.33E+00	1.26E-02	4.43E-04	4.20E-06	4.71E-03	2.24E-05	1.57E-07	7.46E-10	2.28E-02	1.08E-04	4.56E-03	4.33E-03	2.36E-03	1.12E-05	2.36E-06	1.12E-08	3.75E-01	1.78E-03	1.84E-05	8.89E-06	1.49E-02	2.83E-04	4.27E-06	5.40E-09
S32	1.05E+00	4.99E-03	4.38E-03	3.49E-06	2.18E+01	1.03E-01	3.11E-05	7.38E-07	6.54E-01	6.20E-04	3.27E-04	1.15E-07	8.30E-02	3.94E-04	2.24E-04	1.64E-06	2.03E-01	5.78E-04	6.77E-04	9.02E-07	1.36E+00	1.29E-02	4.54E-04	4.31E-06	6.29E-03	2.98E-05	2.10E-07	9.94E-10	2.72E-02	1.29E-04	5.44E-03	5.16E-03	2.20E-03	1.04E-05	2.20E-06	1.04E-08	4.65E-01	2.20E-03	2.28E-05	1.10E-05	1.23E-02	2.33E-04	3.50E-06	4.43E-09
S33	2.01E-01	9.56E-04	8.39E-04	6.69E-07	8.21E+00	3.90E-02	1.17E-05	2.78E-07	7.47E-01	7.09E-04	3.73E-04	1.31E-07	6.65E-02	3.15E-04	1.80E-04	1.31E-06	2.18E-01	6.21E-04	7.27E-04	9.69E-07	1.60E+00	1.51E-02	5.32E-04	5.05E-06	3.46E-03	1.64E-05	1.15E-07	5.47E-10	3.06E-02	1.45E-04	6.13E-03	5.82E-03	2.20E-03	1.04E-05	2.20E-06	1.04E-08	3.87E-01	1.83E-03	1.89E-05	9.17E-06	1.48E-02	2.80E-04	4.22E-06	5.34E-09
S34	3.47E-01	1.65E-03	1.45E-03	1.15E-06	1.13E+01	5.38E-02	1.62E-05	3.84E-07	8.06E-01	7.65E-04	4.03E-04	1.42E-07	7.28E-02	3.45E-04	1.97E-04	1.44E-06	1.94E+00	5.52E-03	6.46E-03	8.61E-06	1.61E+00	1.53E-02	5.37E-04	5.10E-06	3.14E-03	1.49E-05	1.05E-07	4.97E-10	3.39E-02	1.61E-04	6.79E-03	6.44E-03	2.04E-03	9.69E-06	2.04E-06	9.69E-09	4.13E-01	1.96E-03	2.03E-05	9.81E-06	1.79E-02	3.40E-04	5.12E-06	6.48E-09
S35	6.71E-01	3.18E-03	2.79E-03	2.23E-06	1.78E+01	8.47E-02	2.55E-05	6.05E-07	5.12E-01	4.86E-04	2.56E-04	9.01E-08	8.86E-02	4.21E-04	2.40E-04	1.75E-06	2.34E-01	6.65E-04	7.78E-04	1.04E-06	1.01E+00	9.62E-03	3.38E-04	3.21E-06	4.24E-03	2.01E-05	1.41E-07	6.71E-10	1.71E-02	8.13E-05	3.43E-03	3.25E-03	BDL	BDL	BDL	BDL	3.41E-01	1.62E-03	1.67E-05	8.09E-06	1.35E-02	2.57E-04	3.86E-06	4.89E-09
S36	6.40E-01	3.04E-03	2.66E-03	2.12E-06	8.61E+00	4.09E-02	1.23E-05	2.92E-07	6.77E-01	6.43E-04	3.38E-04	1.19E-07	8.22E-02	3.90E-04	2.22E-04	1.63E-06	2.26E-01	6.44E-04	7.54E-04	1.01E-06	1.36E+00	1.29E-02	4.53E-04	4.30E-06	2.51E-03	1.19E-05	8.38E-08	3.98E-10	2.77E-02	1.31E-04	5.53E-03	5.25E-03	2.67E-03	1.27E-05	2.67E-06	1.27E-08	3.66E-01	1.74E-03	1.79E-05	8.68E-06	BDL	BDL	BDL	BDL
S37	6.95E-01	3.30E-03	2.89E-03	2.31E-06	1.37E+01	6.50E-02	1.96E-05	4.64E-07	5.19E-01	4.92E-04	2.59E-04	9.11E-08	7.53E-02	3.57E-04	2.03E-04	1.49E-06	1.71E-01	4.86E-04	5.69E-04	7.58E-07	1.12E+00	1.06E-02	3.72E-04	3.53E-06	1.04E-02	4.92E-05	3.46E-07	1.64E-09	3.05E-02	1.45E-04	6.10E-03	5.79E-03	BDL	BDL	BDL	BDL	1.09E+00	5.16E-03	5.33E-05	2.58E-05	BDL	BDL	BDL	BDL
S38	1.85E+00	8.78E-03	7.71E-03	6.14E-06	1.42E+02	6.76E-01	2.04E-04	4.83E-06	7.37E-01	7.00E-04	3.69E-04	1.30E-07	1.81E-01	8.57E-04	4.88E-04	3.57E-06	2.16E-01	6.14E-04	7.19E-04	9.59E-07	1.30E+00	1.23E-02	4.33E-04	4.11E-06	1.62E-02	7.68E-05	5.40E-07	2.56E-09	1.92E-02	9.10E-05	3.83E-03	3.64E-03	BDL	BDL	BDL	BDL	6.90E-01	3.28E-03	3.38E-05	1.64E-05	3.13E-02	5.94E-04	8.93E-06	1.13E-08
S39	3.24E-01	1.54E-03	1.35E-03	1.08E-06	1.40E+01	6.65E-02	2.00E-05	4.75E-07	7.34E-01	6.96E-04	3.67E-04	1.29E-07	6.36E-02	3.02E-04	1.72E-04	1.26E-06	1.32E-01	3.75E-04	4.39E-04	5.85E-07	1.37E+00	1.30E-02	4.55E-04	4.32E-06	3.46E-03	1.64E-05	1.15E-07	5.47E-10	3.06E-02	1.45E-04	6.13E-03	5.82E-03	1.89E-03	8.95E-06	1.89E-06	8.95E-09	2.79E-01	1.33E-03	1.37E-05	6.63E-06	3.14E-04	5.97E-06	8.98E-08	1.14E-10
S40	4.87E-01	2.31E-03	2.03E-03	1.62E-06	1.09E+01	5.19E-02	1.56E-05	3.70E-07	6.67E-01	6.33E-04	3.33E-04	1.17E-07	1.05E-01	4.99E-04	2.84E-04	2.08E-06	2.07E-01	5.90E-04	6.91E-04	9.21E-07	1.45E+00	1.38E-02	4.85E-04	4.60E-06	5.34E-03	2.54E-05	1.78E-07	8.45E-10	2.77E-02	1.31E-04	5.53E-03	5.25E-03	2.04E-03	9.69E-06	2.04E-06	9.69E-09	7.31E-01	3.47E-03	3.58E-05	1.73E-05	1.26E-02	2.39E-04	3.59E-06	4.55E-09
S41	4.20E-01	1.99E-03	1.75E-03	1.39E-06	1.27E+01	6.03E-02	1.82E-05	4.31E-07	7.55E-01	7.17E-04	3.78E-04	1.33E-07	2.64E-01	1.25E-03	7.14E-04	5.23E-06	2.75E-01	7.84E-04	9.18E-04	1.22E-06	1.51E+00	1.43E-02	5.02E-04	4.76E-06	3.61E-03	1.72E-05	1.20E-07	5.72E-10	3.43E-02	1.63E-04	6.85E-03	6.50E-03	2.20E-03	1.04E-05	2.20E-06	1.04E-08	4.38E-01	2.08E-03	2.15E-05	1.04E-05	1.96E-02	3.73E-04	5.61E-06	7.10E-09
HI			<b>1.58E-01</b>	<b>1.26E-04</b>			<b>1.06E-03</b>	<b>2.52E-05</b>			<b>1.29E-02</b>	<b>4.55E-06</b>			<b>1.29E-02</b>	<b>9.43E-05</b>			<b>3.43E-02</b>	<b>4.57E-05</b>			<b>1.76E-02</b>	<b>1.67E-04</b>			<b>5.40E-06</b>	<b>2.56E-08</b>			<b>2.20E-01</b>	<b>2.08E-01</b>			<b>7.35E-05</b>	<b>3.49E-07</b>			<b>1.60E-03</b>	<b>7.77E-04</b>			<b>1.37E-04</b>	<b>1.73E-07</b>

**Table 4.9: Human health risk assessment indices for  $Exp_{ing}$ ;  $Exp_{der}$ ;  $HQ_{ing}$ ;  $HQ_{der}$  and  $HI$  of studied metals for the Children (Dry season)**

Child Dry	Mn				Fe				Ni				Cu				Zn				Cr				As				Mo				Cd				Ba				Pb							
Springs	Ing	Der	HQ <sub>ing</sub>	HQ <sub>der</sub>	Ing	Der	HQ <sub>ing</sub>	HQ <sub>der</sub>	Ing	Der	HQ <sub>ing</sub>	HQ <sub>der</sub>	Ing	Der	HQ <sub>ing</sub>	HQ <sub>der</sub>	Ing	Der	HQ <sub>ing</sub>	HQ <sub>der</sub>	Ing	Der	HQ <sub>ing</sub>	HQ <sub>der</sub>	Ing	Der	HQ <sub>ing</sub>	HQ <sub>der</sub>	Ing	Der	HQ <sub>ing</sub>	HQ <sub>der</sub>	Ing	Der	HQ <sub>ing</sub>	HQ <sub>der</sub>	Ing	Der	HQ <sub>ing</sub>	HQ <sub>der</sub>	Ing	Der	HQ <sub>ing</sub>	HQ <sub>der</sub>	Ing	Der	HQ <sub>ing</sub>	HQ <sub>der</sub>
S1	1.80E+00	6.62E-03	7.52E-03	4.63E-06	3.77E+01	1.38E-01	5.39E-05	9.88E-07	2.21E+00	1.62E-03	1.10E-03	3.00E-07	6.76E-01	2.48E-03	1.83E-03	1.03E-05	1.40E+00	3.08E-03	4.67E-03	6.23E-06	4.58E+00	3.36E-02	1.53E-03	1.12E-05	8.40E-03	3.08E-05	2.80E-07	1.03E-09	8.88E-02	3.26E-04	4.65E-03	4.41E-03	5.30E-04	1.94E-06	5.30E-07	1.94E-09	1.33E+00	4.89E-03	6.54E-05	2.44E-05	5.64E-02	8.27E-04	1.61E-05	1.58E-08				
S2	9.61E-01	3.52E-03	4.00E-03	2.46E-06	3.18E+01	1.17E-01	4.55E-05	8.34E-07	2.19E+00	1.61E-03	1.10E-03	2.98E-07	3.38E-01	1.24E-03	9.13E-04	5.16E-06	6.76E-01	1.49E-03	2.25E-03	3.00E-06	4.70E+00	3.45E-02	1.57E-03	1.15E-05	1.02E-02	3.74E-05	3.40E-07	1.25E-09	9.60E-02	3.52E-04	5.03E-03	4.77E-03	5.73E-04	2.10E-06	5.73E-07	2.10E-09	2.06E+00	7.54E-03	1.01E-04	3.77E-05	4.92E-02	7.22E-04	1.41E-05	1.37E-08				
S3	9.61E-01	3.52E-03	4.00E-03	2.46E-06	3.11E+01	1.14E-01	4.45E-05	8.16E-07	1.82E+00	1.33E-03	9.09E-04	2.47E-07	3.52E-01	1.29E-03	9.52E-04	5.38E-06	7.37E-01	1.62E-03	2.46E-03	3.27E-06	3.85E+00	2.82E-02	1.28E-03	9.41E-06	8.40E-03	3.08E-05	2.80E-07	1.03E-09	7.56E-02	2.77E-04	3.96E-03	3.76E-03	4.51E-04	1.65E-06	4.51E-07	1.65E-09	2.06E+00	7.54E-03	1.01E-04	3.77E-05	BDL	BDL	BDL	BDL				
S4	1.91E+00	6.99E-03	7.94E-03	4.89E-06	4.57E+01	1.67E-01	6.52E-05	1.20E-06	2.09E+00	1.53E-03	1.04E-03	2.84E-07	1.12E+00	4.11E-03	3.03E-03	1.71E-05	1.09E+00	2.40E-03	3.64E-03	4.85E-06	4.19E+00	3.07E-02	1.40E-03	1.02E-05	8.40E-03	3.08E-05	2.80E-07	1.03E-09	8.04E-02	2.95E-04	4.21E-03	4.00E-03	4.80E-04	1.76E-06	4.80E-07	1.76E-09	1.95E+00	7.17E-03	9.58E-05	3.58E-05	5.52E-02	8.10E-04	1.58E-05	1.54E-08				
S5	1.84E+00	6.76E-03	7.68E-03	4.72E-06	6.66E+01	2.44E-01	9.51E-05	1.74E-06	2.59E+00	1.90E-03	1.30E-03	3.52E-07	7.63E-01	2.80E-03	2.06E-03	1.17E-05	1.10E+00	2.42E-03	3.67E-03	4.89E-06	5.24E+00	3.84E-02	1.75E-03	1.28E-05	8.40E-03	3.08E-05	2.80E-07	1.03E-09	9.18E-02	3.37E-04	4.81E-03	4.56E-03	5.48E-04	2.01E-06	5.48E-07	2.01E-09	9.99E+00	3.66E-02	4.90E-04	1.83E-04	5.64E-02	8.27E-04	1.61E-05	1.58E-08				
S6	1.40E+00	5.13E-03	5.84E-03	3.59E-06	4.14E+01	1.52E-01	5.91E-05	1.08E-06	1.90E+00	1.40E-03	9.52E-04	2.59E-07	7.70E-01	2.82E-03	2.08E-03	1.18E-05	8.11E-01	1.78E-03	2.70E-03	3.61E-06	3.93E+00	2.88E-02	1.31E-03	9.61E-06	BDL	BDL	BDL	BDL	7.50E-02	2.75E-04	3.93E-03	3.73E-03	4.47E-04	1.64E-06	4.47E-07	1.64E-09	1.53E+00	5.61E-03	7.50E-05	2.81E-05	4.80E-02	7.04E-04	1.37E-05	1.34E-08				
S7	1.18E+00	4.33E-03	4.92E-03	3.03E-06	3.22E+01	1.18E-01	4.60E-05	8.43E-07	2.03E+00	1.49E-03	1.01E-03	2.75E-07	6.62E-01	2.43E-03	1.79E-03	1.01E-05	9.78E-01	2.15E-03	3.26E-03	4.35E-06	4.19E+00	3.08E-02	1.40E-03	1.03E-05	8.40E-03	3.08E-05	2.80E-07	1.03E-09	7.68E-02	2.82E-04	4.02E-03	3.82E-03	4.58E-04	1.68E-06	4.58E-07	1.68E-09	1.58E+00	5.80E-03	7.76E-05	2.90E-05	5.52E-02	8.10E-04	1.58E-05	1.54E-08				
S8	1.31E+00	4.81E-03	5.47E-03	3.36E-06	2.59E+01	9.50E-02	3.70E-05	6.79E-07	2.70E+00	1.98E-03	1.35E-03	3.66E-07	3.48E+00	1.27E-02	9.39E-03	5.31E-05	1.73E+00	3.80E-03	5.76E-03	7.68E-06	5.23E+00	3.83E-02	1.74E-03	1.28E-05	7.20E-03	2.64E-05	2.40E-07	8.80E-10	1.15E-01	4.22E-04	6.03E-03	5.73E-03	6.87E-04	2.52E-06	6.87E-07	2.52E-09	6.56E+00	2.40E-02	3.21E-04	1.20E-04	5.16E-02	7.57E-04	1.47E-05	1.44E-08				
S9	1.66E+00	6.09E-03	6.92E-03	4.26E-06	1.83E+01	6.73E-02	2.62E-05	4.80E-07	1.93E+00	1.42E-03	9.66E-04	2.62E-07	5.30E-01	1.94E-03	1.43E-03	8.10E-06	9.28E-01	2.04E-03	3.09E-03	4.12E-06	3.69E+00	2.71E-02	1.23E-03	9.02E-06	9.00E-03	3.30E-05	3.00E-07	1.10E-09	7.14E-02	2.62E-04	3.74E-03	3.55E-03	4.26E-04	1.56E-06	4.26E-07	1.56E-09	6.90E+00	2.53E-02	3.38E-04	1.27E-04	3.14E-01	4.61E-03	8.98E-05	8.78E-08				
S10	1.86E+00	6.82E-03	7.75E-03	4.77E-06	3.13E+01	1.15E-01	4.47E-05	8.19E-07	2.23E+00	1.63E-03	1.11E-03	3.02E-07	1.10E+00	4.03E-03	2.97E-03	1.68E-05	1.33E+00	2.92E-03	4.42E-03	5.90E-06	4.57E+00	3.35E-02	1.52E-03	1.12E-05	1.02E-02	3.74E-05	3.40E-07	1.25E-09	8.94E-02	3.28E-04	4.68E-03	4.44E-03	5.33E-04	1.96E-06	5.33E-07	1.96E-09	1.97E+00	7.21E-03	9.64E-05	3.61E-05	4.80E-02	7.04E-04	1.37E-05	1.34E-08				
S11	1.18E+00	4.34E-03	4.93E-03	3.04E-06	6.21E+01	2.28E-01	8.87E-05	1.63E-06	2.32E+00	1.70E-03	1.16E-03	3.15E-07	4.88E-01	1.79E-03	1.32E-03	7.46E-06	5.75E-01	1.26E-03	1.92E-03	2.55E-06	4.92E+00	3.61E-02	1.64E-03	1.20E-05	1.38E-02	5.06E-05	4.60E-07	1.69E-09	9.12E-02	3.34E-04	4.78E-03	4.53E-03	5.44E-04	1.99E-06	5.44E-07	1.99E-09	5.86E-01	2.15E-03	2.87E-05	1.07E-05	6.48E-02	9.50E-04	1.85E-05	1.81E-08				
S12	8.83E-01	3.24E-03	3.68E-03	2.26E-06	3.68E+01	1.35E-01	5.26E-05	9.64E-07	2.03E+00	1.49E-03	1.02E-03	2.76E-07	3.66E-01	1.34E-03	9.89E-04	5.59E-06	1.00E+00	2.21E-03	3.35E-03	4.46E-06	4.07E+00	2.99E-02	1.36E-03	9.95E-06	8.40E-03	3.08E-05	2.80E-07	1.03E-09	7.80E-02	2.86E-04	4.09E-03	3.88E-03	4.65E-04	1.71E-06	4.65E-07	1.71E-09	1.29E+00	4.71E-03	6.30E-05	2.36E-05	6.12E-02	8.98E-04	1.75E-05	1.71E-08				
S13	1.71E+00	6.29E-03	7.15E-03	4.40E-06	2.79E+01	1.02E-01	3.99E-05	7.31E-07	2.25E+00	1.65E-03	1.13E-03	3.06E-07	3.77E-01	1.38E-03	1.02E-03	5.77E-06	5.71E-01	1.26E-03	1.90E-03	2.54E-06	4.14E+00	3.03E-02	1.38E-03	1.01E-05	1.20E-02	4.40E-05	4.00E-07	1.47E-09	8.64E-02	3.17E-04	4.53E-03	4.30E-03	5.15E-04	1.89E-06	5.15E-07	1.89E-09	4.73E+00	1.73E-02	2.32E-04	8.67E-05	BDL	BDL	BDL	BDL				
S14	1.47E+00	5.38E-03	6.11E-03	3.76E-06	3.65E+01	1.34E-01	5.22E-05	9.56E-07	1.65E+00	1.21E-03	8.26E-04	2.24E-07	6.58E-01	2.41E-03	1.78E-03	1.01E-05	6.77E-01	1.49E-03	2.26E-03	3.01E-06	3.16E+00	2.32E-02	1.05E-03	7.73E-06	8.40E-03	3.08E-05	2.80E-07	1.03E-09	5.94E-02	2.18E-04	3.11E-03	2.95E-03	3.54E-04	1.30E-06	3.54E-07	1.30E-09	1.18E+00	4.32E-03	5.77E-05	2.16E-05	BDL	BDL	BDL	BDL				
S15	8.78E+00	3.22E-02	3.66E-02	2.25E-05	5.35E+01	1.96E-01	7.65E-05	1.40E-06	1.09E+00	8.01E-04	5.46E-04	1.48E-07	3.04E-01	1.11E-03	8.21E-04	4.64E-06	8.63E-01	1.90E-03	2.88E-03	3.83E-06	2.28E+00	1.67E-02	7.60E-04	5.57E-06	9.00E-03	3.30E-05	3.00E-07	1.10E-09	9.12E-02	3.34E-04	4.78E-03	4.53E-03	5.44E-04	1.99E-06	5.44E-07	1.99E-09	1.50E+00	5.51E-03	7.37E-05	2.76E-05	4.92E-02	7.22E-04	1.41E-05	1.37E-08				
S16	8.66E-01	3.18E-03	3.61E-03	2.22E-06	3.34E+01	1.23E-01	4.78E-05	8.76E-07	2.22E+00	1.63E-03	1.11E-03	3.01E-07	3.88E-01	1.42E-03	1.05E-03	5.92E-06	4.62E-01	1.02E-03	1.54E-03	2.05E-06	4.69E+00	3.44E-02	1.56E-03	1.15E-05	1.44E-02	5.28E-05	4.80E-07	1.76E-09	1.12E-01	4.11E-04	5.88E-03	5.58E-03	6.69E-04	2.45E-06	6.69E-07	2.45E-09	3.16E+00	1.16E-02	1.55E-04	5.80E-05	5.16E-02	7.57E-04	1.47E-05	1.44E-08				
S17	1.41E+00	5.18E-03	5.89E-03	3.62E-06	6.76E+01	2.48E-01	9.66E-05	1.77E-06	2.43E+00	1.78E-03	1.22E-03	3.30E-07	4.46E+00	1.63E-02	1.20E-02	6.81E-05	7.21E-01	1.59E-03	2.40E-03	3.21E-06	4.91E+00	3.60E-02	1.64E-03	1.20E-05	1.62E-02	5.94E-05	5.40E-07	1.98E-09	1.27E-01	4.64E-04	6.63E-03	6.29E-03	7.55E-04	2.77E-06	7.55E-07	2.77E-09	4.09E+00	1.50E-02	2.00E-04	7.50E-05	2.32E-01	3.41E-03	6.63E-05	6.49E-08				
S18	1.03E+00	3.76E-03	4.28E-03	2.63E-06	3.28E+01	1.20E-01	4.69E-05	8.60E-07	2.27E+00	1.66E-03	1.13E-03	3.08E-07	3.85E+00	1.41E-02	1.04E-02	5.89E-05	6.29E-01	1.38E-03	2.10E-03	2.79E-06	5.24E+00	3.84E-02	1.75E-03	1.28E-05	1.38E-02	5.06E-05	4.60E-07	1.69E-09	9.78E-02	3.59E-04	5.12E-03	4.86E-03	5.83E-04	2.14E-06	5.83E-07	2.14E-09	7.32E+00	2.68E-02	3.59E-04	1.34E-04	#####	1.53E-02	2.99E-04	2.92E-07				
S19	4.78E-01	1.75E-03	1.99E-03	1.23E-06	2.15E+01	7.87E-02	3.07E-05	5.62E-07	2.10E+00	1.54E-03	1.05E-03	2.85E-07	4.97E-01	1.82E-03	1.34E-03	7.59E-06	6.01E-01	1.32E-03	2.00E-03	2.67E-06	4.38E+00	3.21E-02	1.46E-03	1.07E-05	1.44E-02	5.28E-05	4.80E-07	1.76E-09	9.06E-02	3.32E-04	4.75E-03	4.50E-03	5.40E-04	1.98E-06	5.40E-07	1.98E-09	6.68E+00	2.45E-02	3.28E-04	1.23E-04	5.40E-02	7.92E-04	1.54E-05	1.51E-08				
S20	2.11E+01	7.72E-02	8.77E-02	5.40E-05	3.10E+01	1.14E-01	4.43E-05	8.12E-07	1.99E+00	1.46E-03	9.96E-04	2.70E-07	7.03E-01	2.58E-03	1.90E-03	1.07E-05	9.05E-01	1.99E-03	3.02E-03	4.02E-06	4.04E+00	2.96E-02	1.35E-03	9.86E-06	9.60E-03	3.52E-05	3.20E-07	1.17E-09	8.46E-02	3.10E-04	4.43E-03	4.21E-03	5.05E-04	1.85E-06	5.05E-07	1.85E-09	1.74E+00	6.36E-03	8.51E-05	3.18E-05	5.40E-02	7.92E-04	1.54E-05	1.51E-08				
S21</																																																

S26	2.00E+00	7.32E-03	8.32E-03	5.12E-06	3.63E+01	1.33E-01	5.18E-05	9.50E-07	2.14E+00	1.57E-03	1.07E-03	2.90E-07	4.69E-01	1.72E-03	1.27E-03	7.17E-06	8.08E-01	1.78E-03	2.69E-03	3.59E-06	5.12E+00	3.76E-02	1.71E-03	1.25E-05	7.20E-03	2.64E-05	2.40E-07	8.80E-10	9.36E-02	3.43E-04	4.90E-03	4.65E-03	5.58E-04	2.05E-06	5.58E-07	2.05E-09	1.87E+00	6.87E-03	9.18E-05	3.43E-05	BDL	BDL	BDL	BDL
S27	1.54E+00	5.65E-03	6.43E-03	3.95E-06	3.57E+01	1.31E-01	5.11E-05	9.36E-07	2.21E+00	1.62E-03	1.11E-03	3.00E-07	9.15E-01	3.36E-03	2.47E-03	1.40E-05	1.36E+00	3.00E-03	4.55E-03	6.06E-06	4.41E+00	3.23E-02	1.47E-03	1.08E-05	1.08E-02	3.96E-05	3.60E-07	1.32E-09	8.40E-02	3.08E-04	4.40E-03	4.18E-03	5.01E-04	1.84E-06	5.01E-07	1.84E-09	1.52E+00	5.57E-03	7.45E-05	2.79E-05	5.28E-02	7.74E-04	1.51E-05	1.48E-08
S28	4.89E+00	1.79E-02	2.04E-02	1.25E-05	1.22E+02	4.48E-01	1.74E-04	3.20E-06	2.26E+00	1.66E-03	1.13E-03	3.07E-07	1.95E+00	7.15E-03	5.27E-03	2.98E-05	8.03E-01	1.77E-03	2.68E-03	3.57E-06	4.69E+00	3.44E-02	1.56E-03	1.15E-05	1.08E-02	3.96E-05	3.60E-07	1.32E-09	6.12E-02	2.24E-04	3.21E-03	3.04E-03	3.65E-04	1.34E-06	3.65E-07	1.34E-09	1.74E+00	6.37E-03	8.52E-05	3.19E-05	9.72E-02	1.43E-03	2.78E-05	2.72E-08
S29	5.83E-01	2.14E-03	2.43E-03	1.49E-06	2.16E+01	7.92E-02	3.08E-05	5.65E-07	1.82E+00	1.34E-03	9.12E-04	2.48E-07	4.53E-01	1.66E-03	1.22E-03	6.92E-06	5.95E-01	1.31E-03	1.98E-03	2.64E-06	3.71E+00	2.72E-02	1.24E-03	9.07E-06	BDL	BDL	BDL	BDL	7.20E-02	2.64E-04	3.77E-03	3.58E-03	4.30E-04	1.57E-06	4.30E-07	1.57E-09	1.77E+00	6.49E-03	8.68E-05	3.25E-05	BDL	BDL	BDL	BDL
S30	2.53E+00	9.28E-03	1.05E-02	6.49E-06	1.07E+02	3.93E-01	1.53E-04	2.80E-06	1.93E+00	1.41E-03	9.63E-04	2.62E-07	2.44E+00	8.94E-03	6.59E-03	3.72E-05	7.77E-01	1.71E-03	2.59E-03	3.45E-06	4.18E+00	3.07E-02	1.39E-03	1.02E-05	BDL	BDL	BDL	BDL	6.96E-02	2.55E-04	3.65E-03	3.46E-03	4.15E-04	1.52E-06	4.15E-07	1.52E-09	1.10E+00	4.02E-03	5.37E-05	2.01E-05	4.92E-02	7.22E-04	1.41E-05	1.37E-08
S31	2.64E+00	9.68E-03	1.10E-02	6.77E-06	1.07E+02	3.93E-01	1.53E-04	2.80E-06	1.81E+00	1.33E-03	9.04E-04	2.45E-07	7.82E-01	2.87E-03	2.11E-03	1.20E-05	7.69E-01	1.69E-03	2.56E-03	3.42E-06	4.08E+00	2.99E-02	1.36E-03	9.96E-06	1.26E-02	4.62E-05	4.20E-07	1.54E-09	7.68E-02	2.82E-04	4.02E-03	3.82E-03	4.58E-04	1.68E-06	4.58E-07	1.68E-09	1.08E+00	3.96E-03	5.29E-05	1.98E-05	5.10E-02	7.48E-04	1.46E-05	1.42E-08
S32	3.20E+00	1.17E-02	1.33E-02	8.21E-06	3.58E+01	1.31E-01	5.12E-05	9.39E-07	2.28E+00	1.67E-03	1.14E-03	3.10E-07	4.86E-01	1.78E-03	1.31E-03	7.43E-06	8.26E-01	1.82E-03	2.75E-03	3.67E-06	4.35E+00	3.19E-02	1.45E-03	1.06E-05	BDL	BDL	BDL	BDL	7.98E-02	2.93E-04	4.18E-03	3.97E-03	4.76E-04	1.75E-06	4.76E-07	1.75E-09	8.92E-01	3.27E-03	4.37E-05	1.63E-05	BDL	BDL	BDL	BDL
S33	8.72E-01	3.20E-03	3.63E-03	2.24E-06	2.80E+01	1.03E-01	4.00E-05	7.33E-07	1.98E+00	1.45E-03	9.92E-04	2.69E-07	5.15E-01	1.89E-03	1.39E-03	7.87E-06	6.02E-01	1.32E-03	2.01E-03	2.67E-06	4.04E+00	2.96E-02	1.35E-03	9.87E-06	BDL	BDL	BDL	BDL	7.50E-02	2.75E-04	3.93E-03	3.73E-03	4.47E-04	1.64E-06	4.47E-07	1.64E-09	1.13E+00	4.13E-03	5.52E-05	2.06E-05	BDL	BDL	BDL	BDL
S34	4.88E-01	1.79E-03	2.03E-03	1.25E-06	2.23E+01	8.19E-02	3.19E-05	5.85E-07	2.29E+00	1.68E-03	1.15E-03	3.11E-07	4.58E-01	1.68E-03	1.24E-03	7.00E-06	7.76E-01	1.71E-03	2.59E-03	3.45E-06	4.36E+00	3.20E-02	1.45E-03	1.07E-05	BDL	BDL	BDL	BDL	8.46E-02	3.10E-04	4.43E-03	4.21E-03	5.05E-04	1.85E-06	5.05E-07	1.85E-09	1.67E+00	6.11E-03	8.17E-05	3.06E-05	5.28E-02	7.74E-04	1.51E-05	1.48E-08
S35	1.01E+00	3.70E-03	4.20E-03	2.59E-06	2.67E+01	9.81E-02	3.82E-05	7.01E-07	1.69E+00	1.24E-03	8.45E-04	2.29E-07	5.76E-01	2.11E-03	1.56E-03	8.80E-06	5.27E-01	1.16E-03	1.76E-03	2.34E-06	3.50E+00	2.57E-02	1.17E-03	8.56E-06	BDL	BDL	BDL	BDL	6.54E-02	2.40E-04	3.43E-03	3.25E-03	3.90E-04	1.43E-06	3.90E-07	1.43E-09	9.35E-01	3.43E-03	4.59E-05	1.71E-05	BDL	BDL	BDL	BDL
S36	1.43E+00	5.24E-03	5.95E-03	3.66E-06	3.16E+01	1.16E-01	4.51E-05	8.27E-07	2.37E+00	1.74E-03	1.18E-03	3.22E-07	9.24E-01	3.39E-03	2.50E-03	1.41E-05	1.13E+00	2.49E-03	3.78E-03	5.04E-06	4.77E+00	3.50E-02	1.59E-03	1.17E-05	BDL	BDL	BDL	BDL	9.42E-02	3.45E-04	4.93E-03	4.68E-03	5.62E-04	2.06E-06	5.62E-07	2.06E-09	8.83E-01	3.24E-03	4.33E-05	1.62E-05	7.20E-02	1.06E-03	2.06E-05	2.01E-08
S37	1.30E+00	4.78E-03	5.43E-03	3.34E-06	5.48E+01	2.01E-01	7.83E-05	1.44E-06	2.54E+00	1.87E-03	1.27E-03	3.45E-07	4.72E-01	1.73E-03	1.27E-03	7.21E-06	7.48E-01	1.65E-03	2.49E-03	3.33E-06	5.45E+00	3.99E-02	1.82E-03	1.33E-05	3.60E-02	1.32E-04	1.20E-06	4.40E-09	1.34E-01	4.91E-04	7.01E-03	6.65E-03	7.98E-04	2.93E-06	7.98E-07	2.93E-09	3.77E+00	1.38E-02	1.85E-04	6.91E-05	6.48E-02	9.50E-04	1.85E-05	1.81E-08
S38	1.26E+00	4.62E-03	5.25E-03	3.23E-06	1.14E+02	4.19E-01	1.63E-04	2.99E-06	2.54E+00	1.86E-03	1.27E-03	3.45E-07	8.87E-01	3.25E-03	2.40E-03	1.35E-05	1.01E+00	2.21E-03	3.35E-03	4.47E-06	5.05E+00	3.70E-02	1.68E-03	1.23E-05	1.50E-02	5.50E-05	5.00E-07	1.83E-09	1.03E-01	3.78E-04	5.41E-03	5.13E-03	6.16E-04	2.26E-06	6.16E-07	2.26E-09	1.68E+00	6.14E-03	8.21E-05	3.07E-05	6.36E-02	9.33E-04	1.82E-05	1.78E-08
S39	1.13E+00	4.16E-03	4.73E-03	2.91E-06	3.99E+01	1.46E-01	5.69E-05	1.04E-06	2.39E+00	1.75E-03	1.19E-03	3.24E-07	1.17E+00	4.29E-03	3.16E-03	1.79E-05	1.52E+00	3.35E-03	5.07E-03	6.76E-06	4.54E+00	3.33E-02	1.51E-03	1.11E-05	BDL	BDL	BDL	BDL	9.24E-02	3.39E-04	4.84E-03	4.59E-03	5.51E-04	2.02E-06	5.51E-07	2.02E-09	1.27E+00	4.64E-03	6.21E-05	2.32E-05	5.88E-02	8.62E-04	1.68E-05	1.64E-08
S40	1.23E+00	4.51E-03	5.12E-03	3.15E-06	3.29E+01	1.21E-01	4.71E-05	8.63E-07	2.17E+00	1.59E-03	1.08E-03	2.94E-07	1.20E+00	4.41E-03	3.25E-03	1.84E-05	8.11E-01	1.78E-03	2.70E-03	3.60E-06	4.47E+00	3.28E-02	1.49E-03	1.09E-05	1.56E-02	5.72E-05	5.20E-07	1.91E-09	8.40E-02	3.08E-04	4.40E-03	4.18E-03	5.01E-04	1.84E-06	5.01E-07	1.84E-09	8.95E-01	3.28E-03	4.39E-05	1.64E-05	8.23E-01	1.21E-02	2.35E-04	2.30E-07
S41	9.43E-01	3.46E-03	3.93E-03	2.42E-06	3.38E+01	1.24E-01	4.83E-05	8.86E-07	2.17E+00	1.59E-03	1.09E-03	2.95E-07	8.20E-01	3.01E-03	2.22E-03	1.25E-05	1.12E+00	2.47E-03	3.74E-03	4.98E-06	4.45E+00	3.26E-02	1.48E-03	1.09E-05	9.00E-03	3.30E-05	3.00E-07	1.10E-09	8.64E-02	3.17E-04	4.53E-03	4.30E-03	5.15E-04	1.89E-06	5.15E-07	1.89E-09	8.62E-01	3.16E-03	4.22E-05	1.58E-05	4.80E-02	7.04E-04	1.37E-05	1.34E-08
HI			<b>5.24E-01</b>	<b>3.22E-04</b>			<b>2.56E-03</b>	<b>4.70E-05</b>			<b>4.40E-02</b>	<b>1.19E-05</b>			<b>1.10E-01</b>	<b>6.23E-04</b>			<b>1.24E-01</b>	<b>1.65E-04</b>			<b>5.98E-02</b>	<b>4.39E-04</b>			<b>1.22E-05</b>	<b>4.48E-08</b>			<b>1.92E-01</b>	<b>1.82E-01</b>			<b>2.19E-05</b>	<b>8.02E-08</b>			<b>4.88E-03</b>	<b>1.82E-03</b>			<b>1.15E-03</b>	<b>1.13E-06</b>



**Table 4.10: Human health risk assessment indices for  $Exp_{ing}$ ;  $Exp_{der}$ ;  $HQ_{ing}$ ;  $HQ_{der}$  and  $HI$  of studied metals for the Children (Wet season)**

Child Wet	Mn				Fe				Ni				Cu				Zn				Cr				As				Mo				Cd				Ba				Pb			
Springs	Ing	Der	HQ ing	HQ der	Ing	Der	HQ ing	HQ der	Ing	Der	HQ ing	HQ der	Ing	Der	HQ ing	HQ der	Ing	Der	HQ ing	HQ der	Ing	Der	HQ ing	HQ der	Ing	Ing	Der	Der	Ing	Der	HQ ing	HQ der	Ing	Der	HQ ing	HQ der	Ing	Der	HQ ing	HQ der	Ing	Der	HQ ing	HQ der
S1	2.13E+00	7.82E-03	8.89E-03	5.47E-06	3.23E+01	1.18E-01	4.61E-05	8.45E-07	2.41E+00	1.77E-03	1.21E-03	3.27E-07	2.45E-01	8.98E-04	6.62E-04	3.74E-06	6.07E-01	1.33E-03	2.02E-03	2.70E-06	4.92E+00	3.61E-02	1.64E-03	1.20E-05	1.08E-02	3.96E-05	3.60E-07	1.32E-09	1.01E-01	3.70E-04	5.28E-03	5.01E-03	6.01E-04	2.20E-06	6.01E-07	2.20E-09	1.76E+00	6.47E-03	8.64E-05	3.23E-05	BDL	BDL	BDL	BDL
S2	1.58E+01	5.78E-02	6.57E-02	4.04E-05	2.09E+02	7.65E-01	2.98E-04	5.46E-06	2.34E+00	1.71E-03	1.17E-03	3.18E-07	5.60E-01	2.05E-03	1.51E-03	8.55E-06	6.31E-01	1.39E-03	2.10E-03	2.81E-06	5.03E+00	3.69E-02	1.68E-03	1.23E-05	1.62E-02	5.94E-05	5.40E-07	1.98E-09	9.12E-02	3.34E-04	4.78E-03	4.53E-03	5.44E-04	1.99E-06	5.44E-07	1.99E-09	2.01E+00	7.38E-03	9.86E-05	3.69E-05	8.76E-02	1.28E-03	2.50E-05	2.45E-08
S3	4.97E+00	1.82E-02	2.07E-02	1.27E-05	1.37E+02	5.03E-01	1.96E-04	3.59E-06	2.16E+00	1.59E-03	1.08E-03	2.94E-07	4.95E-01	1.82E-03	1.34E-03	7.56E-06	5.13E-01	1.13E-03	1.71E-03	2.28E-06	4.55E+00	3.33E-02	1.52E-03	1.11E-05	9.00E-03	3.30E-05	3.00E-07	1.10E-09	8.28E-02	3.04E-04	4.34E-03	4.12E-03	4.94E-04	1.81E-06	4.94E-07	1.81E-09	2.11E+00	7.73E-03	1.03E-04	3.87E-05	5.04E-02	7.39E-04	1.44E-05	1.41E-08
S4	2.52E+00	9.23E-03	1.05E-02	6.45E-06	4.92E+01	1.81E-01	7.03E-05	1.29E-06	2.26E+00	1.66E-03	1.13E-03	3.07E-07	3.10E-01	1.14E-03	8.37E-04	4.73E-06	5.66E-01	1.24E-03	1.89E-03	2.51E-06	4.62E+00	3.39E-02	1.54E-03	1.13E-05	1.44E-02	5.28E-05	4.80E-07	1.76E-09	9.48E-02	3.48E-04	4.97E-03	4.71E-03	5.66E-04	2.07E-06	5.66E-07	2.07E-09	1.97E+00	7.21E-03	9.64E-05	3.60E-05	BDL	BDL	BDL	BDL
S5	1.23E+00	4.52E-03	5.14E-03	3.16E-06	3.71E+01	1.36E-01	5.30E-05	9.72E-07	2.46E+00	1.80E-03	1.23E-03	3.34E-07	3.96E-01	1.45E-03	1.07E-03	6.05E-06	5.55E-01	1.22E-03	1.85E-03	2.47E-06	4.79E+00	3.51E-02	1.60E-03	1.17E-05	8.40E-03	3.08E-05	2.80E-07	1.03E-09	9.48E-02	3.48E-04	4.97E-03	4.71E-03	5.66E-04	2.07E-06	5.66E-07	2.07E-09	1.03E+01	3.76E-02	5.03E-04	1.88E-04	6.84E-02	1.00E-03	1.95E-05	1.91E-08
S6	2.19E+00	8.01E-03	9.11E-03	5.60E-06	3.93E+01	1.44E-01	5.62E-05	1.03E-06	2.24E+00	1.64E-03	1.12E-03	3.05E-07	2.28E-01	8.36E-04	6.16E-04	3.48E-06	6.26E-01	1.38E-03	2.09E-03	2.78E-06	4.87E+00	3.57E-02	1.62E-03	1.19E-05	1.50E-02	5.50E-05	5.00E-07	1.83E-09	9.78E-02	3.59E-04	5.12E-03	4.86E-03	5.83E-04	2.14E-06	5.83E-07	2.14E-09	2.06E+00	7.54E-03	1.01E-04	3.77E-05	4.68E-02	6.86E-04	1.34E-05	1.31E-08
S7	3.58E+01	1.31E-01	1.49E-01	9.18E-05	5.76E+01	2.11E-01	8.22E-05	1.51E-06	2.10E+00	1.54E-03	1.05E-03	2.86E-07	2.66E-01	9.75E-04	7.18E-04	4.06E-06	6.29E-01	1.38E-03	2.10E-03	2.79E-06	4.48E+00	3.29E-02	1.49E-03	1.10E-05	8.40E-03	3.08E-05	2.80E-07	1.03E-09	8.94E-02	3.28E-04	4.68E-03	4.44E-03	5.33E-04	1.96E-06	5.33E-07	1.96E-09	2.11E+00	7.74E-03	1.03E-04	3.87E-05	BDL	BDL	BDL	BDL
S8	1.26E+00	4.62E-03	5.26E-03	3.23E-06	4.64E+01	1.70E-01	6.63E-05	1.21E-06	3.29E+00	2.41E-03	1.64E-03	4.46E-07	3.21E-01	1.18E-03	8.68E-04	4.90E-06	7.90E-01	1.74E-03	2.63E-03	3.51E-06	6.36E+00	4.67E-02	2.12E-03	1.56E-05	1.50E-02	5.50E-05	5.00E-07	1.83E-09	1.28E-01	4.69E-04	6.69E-03	6.35E-03	7.62E-04	2.80E-06	7.62E-07	2.80E-09	6.45E+00	2.36E-02	3.16E-04	1.18E-04	6.72E-02	9.86E-04	1.92E-05	1.88E-08
S9	1.72E+00	6.31E-03	7.17E-03	4.41E-06	7.38E+01	2.71E-01	1.05E-04	1.93E-06	2.33E+00	1.71E-03	1.17E-03	3.17E-07	6.63E-01	2.43E-03	1.79E-03	1.01E-05	1.60E+00	3.52E-03	5.33E-03	7.11E-06	4.84E+00	3.55E-02	1.61E-03	1.18E-05	1.62E-02	5.94E-05	5.40E-07	1.98E-09	9.48E-02	3.48E-04	4.97E-03	4.71E-03	5.66E-04	2.07E-06	5.66E-07	2.07E-09	9.29E+00	3.41E-02	4.55E-04	1.70E-04	6.96E-02	1.02E-03	1.99E-05	1.94E-08
S10	1.64E+00	6.01E-03	6.83E-03	4.20E-06	3.71E+01	1.36E-01	5.31E-05	9.73E-07	2.34E+00	1.72E-03	1.17E-03	3.18E-07	8.33E-01	3.05E-03	2.25E-03	1.27E-05	1.12E+00	2.47E-03	3.74E-03	4.99E-06	4.73E+00	3.47E-02	1.58E-03	1.16E-05	1.20E-02	4.40E-05	4.00E-07	1.47E-09	9.30E-02	3.41E-04	4.87E-03	4.62E-03	5.55E-04	2.03E-06	5.55E-07	2.03E-09	2.98E+00	1.09E-02	1.46E-04	5.47E-05	6.00E-02	8.80E-04	1.71E-05	1.68E-08
S11	1.00E+00	3.68E-03	4.19E-03	2.58E-06	6.26E+01	2.30E-01	8.94E-05	1.64E-06	2.52E+00	1.85E-03	1.26E-03	3.43E-07	3.42E-01	1.25E-03	9.24E-04	5.23E-06	4.44E-01	9.77E-04	1.48E-03	1.97E-06	5.16E+00	3.78E-02	1.72E-03	1.26E-05	1.44E-02	5.28E-05	4.80E-07	1.76E-09	1.07E-01	3.92E-04	5.59E-03	5.31E-03	6.37E-04	2.34E-06	6.37E-07	2.34E-09	8.24E-01	3.02E-02	4.04E-05	1.51E-05	5.34E-02	7.83E-04	1.53E-05	1.49E-08
S12	1.10E+00	4.03E-03	4.58E-03	2.82E-06	5.12E+01	1.88E-01	7.32E-05	1.34E-06	3.20E+00	2.34E-03	1.60E-03	4.34E-07	3.14E-01	1.15E-03	8.48E-04	4.79E-06	8.78E-01	1.93E-03	2.93E-03	3.90E-06	6.11E+00	4.48E-02	2.04E-03	1.49E-05	1.26E-02	4.62E-05	4.20E-07	1.54E-09	1.29E-01	4.73E-04	6.76E-03	6.41E-03	7.70E-04	2.82E-06	7.70E-07	2.82E-09	2.10E+00	7.69E-03	1.03E-04	3.84E-05	5.64E-02	8.27E-04	1.61E-05	1.58E-08
S13	1.17E+00	4.28E-03	4.86E-03	2.99E-06	3.93E+01	1.44E-01	5.62E-05	1.03E-06	2.62E+00	1.92E-03	1.31E-03	3.56E-07	2.05E-01	7.50E-04	5.53E-04	3.13E-06	6.05E-01	1.33E-03	2.02E-03	2.69E-06	4.39E+00	3.22E-02	1.46E-03	1.07E-05	9.60E-03	3.52E-05	3.20E-07	1.17E-09	9.00E-02	3.30E-04	4.71E-03	4.47E-03	5.37E-04	1.97E-06	5.37E-07	1.97E-09	7.30E+00	2.68E-02	3.58E-04	1.34E-04	BDL	BDL	BDL	BDL
S14	8.42E-01	3.09E-03	3.51E-03	2.16E-06	3.18E+01	1.17E-01	4.54E-05	8.33E-07	2.40E+00	1.76E-03	1.20E-03	3.26E-07	2.39E-01	8.76E-04	6.45E-04	3.65E-06	7.69E-01	1.69E-03	2.56E-03	3.42E-06	4.88E+00	3.58E-02	1.63E-03	1.19E-05	1.08E-02	3.96E-05	3.60E-07	1.32E-09	9.42E-02	3.45E-04	4.93E-03	4.68E-03	5.62E-04	2.06E-06	5.62E-07	2.06E-09	1.44E+00	5.29E-03	7.07E-05	2.65E-05	BDL	BDL	BDL	BDL
S15	5.75E+00	2.11E-02	2.40E-02	1.47E-05	1.01E+02	3.70E-01	1.44E-04	2.64E-06	2.05E+00	1.50E-03	1.02E-03	2.78E-07	3.76E-01	1.38E-03	1.02E-03	5.75E-06	6.57E-01	1.45E-03	2.19E-03	2.92E-06	4.20E+00	3.08E-02	1.40E-03	1.03E-05	1.26E-02	4.62E-05	4.20E-07	1.54E-09	8.46E-02	3.10E-04	4.43E-03	4.21E-03	5.05E-04	1.85E-06	5.05E-07	1.85E-09	1.71E+00	6.27E-03	8.38E-05	3.13E-05	1.01E-01	1.48E-03	2.88E-05	2.82E-08
S16	7.67E-01	2.81E-03	3.20E-03	1.97E-06	4.23E+01	1.55E-01	6.05E-05	1.11E-06	1.98E+00	1.45E-03	9.88E-04	2.68E-07	2.15E-01	7.88E-04	5.81E-04	3.28E-06	4.61E-01	1.01E-03	1.54E-03	2.05E-06	4.16E+00	3.05E-02	1.39E-03	1.02E-05	1.62E-02	5.94E-05	5.40E-07	1.98E-09	1.09E-01	3.98E-04	5.69E-03	5.40E-03	6.48E-04	2.38E-06	6.48E-07	2.38E-09	3.46E+00	1.27E-02	1.70E-04	6.35E-05	BDL	BDL	BDL	BDL
S17	2.33E+00	8.53E-03	9.70E-03	5.97E-06	9.09E+01	3.33E-01	1.30E-04	2.38E-06	2.22E+00	1.63E-03	1.11E-03	3.01E-07	2.27E-01	8.34E-04	6.15E-04	3.47E-06	5.35E-01	1.18E-03	1.78E-03	2.38E-06	4.76E+00	3.49E-02	1.59E-03	1.16E-05	1.38E-02	5.06E-05	4.60E-07	1.69E-09	1.30E-01	4.77E-04	6.82E-03	6.47E-03	7.77E-04	2.85E-06	7.77E-07	2.85E-09	4.02E+00	1.48E-02	1.97E-04	7.38E-05	6.60E-02	9.68E-04	1.89E-05	1.84E-08
S18	1.41E+00	5.17E-03	5.87E-03	3.61E-06	1.04E+02	3.82E-01	1.49E-04	2.73E-06	2.52E+00	1.85E-03	1.26E-03	3.43E-07	3.35E-01	1.23E-03	9.05E-04	5.12E-06	5.87E-01	1.29E-03	1.96E-03	2.61E-06	5.89E+00	4.32E-02	1.96E-03	1.44E-05	1.50E-02	5.50E-05	5.00E-07	1.83E-09	1.11E-01	4.07E-04	5.81E-03	5.52E-03	6.62E-04	2.43E-06	6.62E-07	2.43E-09	9.31E+00	3.41E-02	4.57E-04	1.71E-04	1.49E-01	2.19E-03	4.27E-05	4.17E-08
S19	5.55E-01	2.04E-03	2.31E-03	1.42E-06	2.30E+01	8.45E-02	3.29E-05	6.03E-07	2.02E+00	1.48E-03	1.01E-03	2.74E-07	1.52E-01	5.59E-04	4.12E-04	2.33E-06	7.41E-01	1.63E-03	2.47E-03	3.29E-06	4.21E+00	3.09E-02	1.40E-03	1.03E-05	1.20E-02	4.40E-05	4.00E-07	1.47E-09	8.82E-02	3.23E-04	4.62E-03	4.38E-03	5.26E-04	1.93E-06	5.26E-07	1.93E-09	8.45E+00	3.10E-02	4.14E-04	1.55E-04	BDL	BDL	BDL	BDL
S20	5.05E+00	1.85E-02	2.10E-02	1.29E-05	7.27E+01	2.67E-01	1.04E-04	1.90E-06	1.77E+00	1.30E-03	8.87E-04	2.41E-07	2.77E-01	1.02E-03	7.49E-04	4.24E-06	4.54E-01	9.98E-04	1.51E-03	2.02E-06	3.58E+00	2.62E-02	1.19E-03	8.75E-06	9.60E-03	3.52E-05	3.20E-07	1.17E-09	7.20E-02	2.64E-04	3.77E-03	3.58E-03	4.30E-04	1.57E-06	4.30E-07	1.57E-09	3.58E+00	1.31E-02	1.75E-04	6.56E-05	BDL	BDL	BDL	BDL
S21	8.75E+00	3.21E-02	3.65E-02	2.24E-05	3.23E+01	1.18E																																						

S26	1.54E+00	5.65E-03	6.43E-03	3.95E-06	2.96E+01	1.09E-01	4.23E-05	7.76E-07	2.37E+00	1.74E-03	1.18E-03	3.21E-07	1.95E-01	7.15E-04	5.27E-04	2.98E-06	4.71E-01	1.04E-03	1.57E-03	2.09E-06	5.07E+00	3.72E-02	1.69E-03	1.24E-05	8.40E-03	3.08E-05	2.80E-07	1.03E-09	9.90E-02	3.63E-04	5.19E-03	4.92E-03	5.91E-04	2.17E-06	5.91E-07	2.17E-09	1.92E+00	7.03E-03	9.40E-05	3.51E-05	4.80E-02	7.04E-04	1.37E-05	1.34E-08
S27	1.96E+00	7.20E-03	8.18E-03	5.04E-06	3.88E+01	1.42E-01	5.55E-05	1.02E-06	2.41E+00	1.77E-03	1.20E-03	3.27E-07	3.07E-01	1.13E-03	8.30E-04	4.69E-06	7.94E-01	1.75E-03	2.65E-03	3.53E-06	5.11E+00	3.75E-02	1.70E-03	1.25E-05	1.26E-02	4.62E-05	4.20E-07	1.54E-09	1.00E-01	3.67E-04	5.25E-03	4.98E-03	5.98E-04	2.19E-06	5.98E-07	2.19E-09	2.10E+00	7.68E-03	1.03E-04	3.84E-05	4.92E-02	7.22E-04	1.41E-05	1.37E-08
S28	1.26E+00	4.62E-03	5.26E-03	3.23E-06	4.38E+01	1.61E-01	6.26E-05	1.15E-06	2.20E+00	1.61E-03	1.10E-03	2.98E-07	2.23E-01	8.18E-04	6.03E-04	3.41E-06	5.27E-01	1.16E-03	1.76E-03	2.34E-06	4.66E+00	3.42E-02	1.55E-03	1.14E-05	1.20E-02	4.40E-05	4.00E-07	1.47E-09	8.70E-02	3.19E-04	4.56E-03	4.33E-03	5.19E-04	1.90E-06	5.19E-07	1.90E-09	1.89E+00	6.93E-03	9.27E-05	3.47E-05	BDL	BDL	BDL	BDL
S29	1.52E+00	5.58E-03	6.34E-03	3.90E-06	4.66E+01	1.71E-01	6.65E-05	1.22E-06	2.77E+00	2.03E-03	1.38E-03	3.76E-07	3.53E-01	1.29E-03	9.54E-04	5.39E-06	1.04E+00	2.28E-03	3.45E-03	4.61E-06	5.87E+00	4.30E-02	1.96E-03	1.43E-05	9.60E-03	3.52E-05	3.20E-07	1.17E-09	1.16E-01	4.25E-04	6.07E-03	5.76E-03	6.91E-04	2.53E-06	6.91E-07	2.53E-09	1.34E+00	4.93E-03	6.59E-05	2.46E-05	6.00E-02	8.80E-04	1.71E-05	1.68E-08
S30	1.77E+00	6.49E-03	7.38E-03	4.54E-06	2.86E+01	1.05E-01	4.08E-05	7.48E-07	1.73E+00	1.27E-03	8.66E-04	2.35E-07	9.21E-01	3.38E-03	2.49E-03	1.41E-05	8.74E-01	1.92E-03	2.91E-03	3.88E-06	3.75E+00	2.75E-02	1.25E-03	9.17E-06	8.00E-03	2.93E-05	2.67E-07	9.78E-10	7.20E-02	2.64E-04	3.77E-03	3.58E-03	4.30E-04	1.57E-06	4.30E-07	1.57E-09	1.69E+00	6.21E-03	8.30E-05	3.10E-05	5.04E-02	7.39E-04	1.44E-05	1.41E-08
S31	2.39E+00	8.76E-03	9.96E-03	6.13E-06	7.31E+01	2.68E-01	1.04E-04	1.91E-06	2.35E+00	1.72E-03	1.18E-03	3.19E-07	3.98E-01	1.46E-03	1.08E-03	6.08E-06	7.56E-01	1.66E-03	2.52E-03	3.36E-06	5.07E+00	3.72E-02	1.69E-03	1.24E-05	1.80E-02	6.60E-05	6.00E-07	2.20E-09	8.70E-02	3.19E-04	4.56E-03	4.33E-03	5.19E-04	1.90E-06	5.19E-07	1.90E-09	1.43E+00	5.25E-03	7.01E-05	2.62E-05	5.70E-02	8.36E-04	1.63E-05	1.59E-08
S32	4.01E+00	1.47E-02	1.67E-02	1.03E-05	8.31E+01	3.05E-01	1.19E-04	2.18E-06	2.50E+00	1.83E-03	1.25E-03	3.39E-07	3.17E-01	1.16E-03	8.56E-04	4.84E-06	7.75E-01	1.71E-03	2.58E-03	3.45E-06	5.20E+00	3.81E-02	1.73E-03	1.27E-05	2.40E-02	8.80E-05	8.00E-07	2.93E-09	1.04E-01	3.81E-04	5.44E-03	5.16E-03	6.19E-04	2.27E-06	6.19E-07	2.27E-09	1.77E+00	6.50E-03	8.69E-05	3.25E-05	4.68E-02	6.86E-04	1.34E-05	1.31E-08
S33	7.69E-01	2.82E-03	3.21E-03	1.97E-06	3.13E+01	1.15E-01	4.48E-05	8.21E-07	2.85E+00	2.09E-03	1.43E-03	3.87E-07	2.54E-01	9.31E-04	6.86E-04	3.88E-06	8.33E-01	1.83E-03	2.78E-03	3.70E-06	6.09E+00	4.47E-02	2.03E-03	1.49E-05	1.32E-02	4.84E-05	4.40E-07	1.61E-09	1.17E-01	4.29E-04	6.13E-03	5.82E-03	6.98E-04	2.56E-06	6.98E-07	2.56E-09	1.48E+00	5.41E-03	7.24E-05	2.71E-05	5.64E-02	8.27E-04	1.61E-05	1.58E-08
S34	1.32E+00	4.86E-03	5.52E-03	3.40E-06	4.32E+01	1.59E-01	6.18E-05	1.13E-06	3.08E+00	2.26E-03	1.54E-03	4.18E-07	2.78E-01	1.02E-03	7.51E-04	4.24E-06	7.40E+00	1.63E-02	2.47E-02	3.29E-05	6.15E+00	4.51E-02	2.05E-03	1.50E-05	1.20E-02	4.40E-05	4.00E-07	1.47E-09	1.30E-01	4.75E-04	6.79E-03	6.44E-03	7.73E-04	2.83E-06	7.73E-07	2.83E-09	1.58E+00	5.79E-03	7.74E-05	2.89E-05	6.84E-02	1.00E-03	1.95E-05	1.91E-08
S35	2.56E+00	9.39E-03	1.07E-02	6.56E-06	6.81E+01	2.50E-01	9.73E-05	1.78E-06	1.96E+00	1.43E-03	9.78E-04	2.66E-07	3.38E-01	1.24E-03	9.15E-04	5.17E-06	8.92E-01	1.96E-03	2.97E-03	3.96E-06	3.87E+00	2.84E-02	1.29E-03	9.46E-06	1.62E-02	5.94E-05	5.40E-07	1.98E-09	6.54E-02	2.40E-04	3.43E-03	3.25E-03	3.90E-04	1.43E-06	3.90E-07	1.43E-09	1.30E+00	4.78E-03	6.39E-05	2.39E-05	5.16E-02	7.57E-04	1.47E-05	1.44E-08
S36	2.44E+00	8.95E-03	1.02E-02	6.26E-06	3.29E+01	1.21E-01	4.70E-05	8.61E-07	2.58E+00	1.90E-03	1.29E-03	3.51E-07	3.14E-01	1.15E-03	8.48E-04	4.79E-06	8.64E-01	1.90E-03	2.88E-03	3.84E-06	5.19E+00	3.81E-02	1.73E-03	1.27E-05	9.60E-03	3.52E-05	3.20E-07	1.17E-09	1.06E-01	3.87E-04	5.53E-03	5.25E-03	6.30E-04	2.31E-06	6.30E-07	2.31E-09	1.40E+00	5.12E-03	6.84E-05	2.56E-05	BDL	BDL	BDL	BDL
S37	2.65E+00	9.73E-03	1.11E-02	6.80E-06	5.23E+01	1.92E-01	7.47E-05	1.37E-06	1.98E+00	1.45E-03	9.90E-04	2.69E-07	2.87E-01	1.05E-03	7.77E-04	4.39E-06	6.52E-01	1.43E-03	2.17E-03	2.90E-06	4.26E+00	3.13E-02	1.42E-03	1.04E-05	3.96E-02	1.45E-04	1.32E-06	4.84E-09	1.16E-01	4.27E-04	6.10E-03	5.79E-03	6.94E-04	2.55E-06	6.94E-07	2.55E-09	4.15E+00	1.52E-02	2.03E-04	7.61E-05	BDL	BDL	BDL	BDL
S38	7.06E+00	2.59E-02	2.94E-02	1.81E-05	5.44E+02	1.99E+00	7.77E-04	1.42E-05	2.82E+00	2.06E-03	1.41E-03	3.82E-07	6.89E-01	2.53E-03	1.86E-03	1.05E-05	8.24E-01	1.81E-03	2.75E-03	3.66E-06	4.96E+00	3.64E-02	1.65E-03	1.21E-05	6.18E-02	2.27E-06	2.06E-06	7.55E-09	7.32E-02	2.68E-04	3.83E-03	3.64E-03	4.37E-04	1.60E-06	4.37E-07	1.60E-09	2.64E+00	9.67E-03	1.29E-04	4.83E-05	1.19E-01	1.75E-03	3.41E-05	3.34E-08
S39	1.24E+00	4.54E-03	5.16E-03	3.17E-06	5.35E+01	1.96E-01	7.64E-05	1.40E-06	2.80E+00	2.05E-03	1.40E-03	3.80E-07	2.43E-01	8.91E-04	6.57E-04	3.71E-06	5.03E-01	1.11E-03	1.68E-03	2.23E-06	5.21E+00	3.82E-02	1.74E-03	1.27E-05	1.32E-02	4.84E-05	4.40E-07	1.61E-09	1.17E-01	4.29E-04	6.13E-03	5.82E-03	6.98E-04	2.56E-06	6.98E-07	2.56E-09	1.07E+00	3.91E-03	5.23E-05	1.95E-05	1.20E-03	1.76E-05	3.43E-07	3.35E-10
S40	1.86E+00	6.82E-03	7.75E-03	4.77E-06	4.17E+01	1.53E-01	5.96E-05	1.09E-06	2.55E+00	1.87E-03	1.27E-03	3.46E-07	4.01E-01	1.47E-03	1.08E-03	6.13E-06	7.91E-01	1.74E-03	2.64E-03	3.52E-06	5.55E+00	4.07E-02	1.85E-03	1.36E-05	2.04E-02	7.48E-05	6.80E-07	2.49E-09	1.06E-01	3.87E-04	5.53E-03	5.25E-03	6.30E-04	2.31E-06	6.30E-07	2.31E-09	2.79E+00	1.02E-02	1.37E-04	5.12E-05	4.80E-02	7.04E-04	1.37E-05	1.34E-08
S41	1.60E+00	5.88E-03	6.68E-03	4.11E-06	4.85E+01	1.78E-01	6.93E-05	1.27E-06	2.88E+00	2.12E-03	1.44E-03	3.92E-07	1.01E+00	3.70E-03	2.73E-03	1.54E-05	1.05E+00	2.31E-03	3.50E-03	4.67E-06	5.75E+00	4.22E-02	1.92E-03	1.41E-05	1.38E-02	5.06E-05	4.60E-07	1.69E-09	1.31E-01	4.80E-04	6.85E-03	6.50E-03	7.80E-04	2.86E-06	7.80E-07	2.86E-09	1.67E+00	6.14E-03	8.20E-05	3.07E-05	7.50E-02	1.10E-03	2.14E-05	2.10E-08
HI			<b>6.03E-01</b>	<b>3.71E-04</b>			<b>4.05E-03</b>	<b>7.43E-05</b>			<b>4.94E-02</b>	<b>1.34E-05</b>			<b>4.92E-02</b>	<b>2.78E-04</b>			<b>1.31E-01</b>	<b>1.74E-04</b>			<b>6.74E-02</b>	<b>4.94E-04</b>			<b>2.06E-05</b>	<b>7.56E-08</b>			<b>2.20E-01</b>	<b>2.08E-01</b>			<b>2.50E-05</b>	<b>9.17E-08</b>			<b>6.13E-03</b>	<b>2.29E-03</b>			<b>5.22E-04</b>	<b>5.11E-07</b>

#### 4.6.2 Carcinogenic Risk Analysis

Cancer Risk (CR) is determined as the probability of a human developing cancer over a long period, because of exposure to a potential carcinogen (WHO, 2013).

Trace elements such as As, Cr, Pb and Ni can enhance or cause cancer growth in humans (Cao et al., 2014). Long term exposure to trace elements has an impact on human health as it could result in various types of cancers, if the level is high. Pb, Cr, Cd, and Ni are known as cancer-causing agents. The possibility of cancer risk was computed using those metals' levels in the spring water samples. The cancer-causing hazard appraisal for adults and children is given in (Table 4.11). For one metal, CR over  $1 \times 10^{-6}$  is considered as not significant and the Cancer Risk can be ignored, while CR below  $1 \times 10^{-4}$  is considered as dangerous, therefore, harmful. The results of CR for children, both in the wet and the dry seasons, were higher by at least 60% as compared to adults. The degree of CR trace elements were in the order of Cr>Pb>Ni>Cd (Table 4.11).

Insignificant cancer risk from the consumption of the water were recorded for Cd; this was due to its low levels obtained in the water samples. Ni also recorded acceptable levels for adults in both seasons, however, the levels of Ni computed are of concern for children. Both Cr and Pb computed risk values higher than the threshold levels of  $1 \times 10^{-4}$  for both adults and children. This shows that the consumption of this water continuously does have a cancer risk. The cancer risk index was designed to prevent any likelihood of adverse effects on humans using a very strict method of computation. The residents of these villages, however, use different sources of water, such as the rains and boreholes; they do not rely solely on the spring water, thereby, reducing the chances of cancer occurrences in the community.

**Table 4.11: Recorded data of Cancer Risk for both adult and children (dry and wet season)**

sampling points	CR				CR				CR				CR			
	Adult dry				Adult Wet				Child Dry				Child Wet			
	<i>Ni</i>	<i>Cr</i>	<i>Cd</i>	<i>Pb</i>	<i>Ni</i>	<i>Cr</i>	<i>Cd</i>	<i>Pb</i>	<i>Ni</i>	<i>Cr</i>	<i>Cd</i>	<i>Pb</i>	<i>Ni</i>	<i>Cr</i>	<i>Cd</i>	<i>Pb</i>
S1	6.35E-04	2.40E-03	3.35E-07	1.74E-03	6.64E-04	2.49E-03	3.48E-07	1.74E-03	2.43E-03	9.17E-03	1.28E-06	6.64E-03	2.54E-03	9.48E-03	1.33E-06	6.64E-03
S2	6.31E-04	2.46E-03	3.61E-07	1.52E-03	5.73E-04	2.55E-03	3.74E-07	2.11E-03	2.41E-03	9.41E-03	1.38E-06	5.79E-03	2.19E-03	9.72E-03	1.43E-06	8.05E-03
S3	5.23E-04	2.02E-03	BDL	BDL	6.26E-04	2.20E-03	3.09E-07	1.55E-03	2.00E-03	7.70E-03	BDL	BDL	2.39E-03	8.40E-03	1.18E-06	5.93E-03
S4	6.01E-04	2.19E-03	3.61E-07	1.70E-03	6.26E-04	2.31E-03	4.89E-07	1.70E-03	2.30E-03	8.38E-03	1.38E-06	6.49E-03	2.39E-03	8.81E-03	1.87E-06	6.49E-03
S5	7.47E-04	2.75E-03	3.35E-07	1.74E-03	7.27E-04	2.63E-03	3.35E-07	1.92E-03	2.85E-03	1.05E-02	1.28E-06	6.64E-03	2.78E-03	1.00E-02	1.28E-06	7.34E-03
S6	5.48E-04	2.06E-03	BDL	1.48E-03	5.97E-04	2.31E-03	3.09E-07	1.46E-03	2.09E-03	7.87E-03	BDL	5.65E-03	2.28E-03	8.78E-03	1.18E-06	5.58E-03
S7	7.76E-04	2.20E-03	3.09E-07	1.70E-03	5.95E-04	2.27E-03	3.09E-07	1.70E-03	2.23E-03	8.39E-03	1.18E-06	6.49E-03	2.27E-03	8.67E-03	1.18E-06	6.49E-03
S8	5.56E-04	2.74E-03	3.61E-07	1.59E-03	8.61E-04	3.03E-03	4.38E-07	3.51E-02	2.96E-03	1.05E-02	1.38E-06	6.07E-03	3.29E-03	1.16E-02	1.67E-06	6.99E-03
S9	6.41E-04	1.93E-03	3.09E-07	9.69E-03	6.14E-04	2.23E-03	3.09E-07	5.92E-03	2.12E-03	7.38E-03	1.18E-06	3.70E-02	2.34E-03	8.53E-03	1.18E-06	2.26E-02
S10	6.69E-04	2.39E-03	BDL	1.48E-03	6.57E-04	2.44E-03	3.61E-07	1.66E-03	2.45E-03	9.13E-03	BDL	5.65E-03	2.51E-03	9.30E-03	1.38E-06	6.35E-03
S11	5.85E-04	2.58E-03	BDL	2.00E-03	6.97E-04	2.64E-03	3.61E-07	1.81E-03	2.55E-03	9.84E-03	BDL	7.62E-03	2.66E-03	1.01E-02	1.38E-06	6.95E-03
S12	6.49E-04	2.13E-03	3.61E-07	1.89E-03	7.52E-04	2.67E-03	3.74E-07	1.81E-03	2.23E-03	8.14E-03	1.38E-06	7.20E-03	2.87E-03	1.02E-02	1.43E-06	6.92E-03
S13	4.75E-04	2.17E-03	3.09E-07	BDL	7.03E-04	2.23E-03	3.09E-07	BDL	2.48E-03	8.27E-03	1.18E-06	BDL	2.68E-03	8.53E-03	1.18E-06	BDL
S14	3.14E-04	1.66E-03	BDL	BDL	5.83E-04	2.11E-03	3.09E-07	BDL	1.82E-03	6.33E-03	BDL	BDL	3.54E-03	8.04E-03	1.18E-06	BDL
S15	6.38E-04	1.19E-03	BDL	1.52E-03	4.52E-04	1.70E-03	BDL	2.31E-03	1.20E-03	4.56E-03	BDL	5.79E-03	1.72E-03	6.48E-03	BDL	8.82E-03
S16	6.99E-04	2.46E-03	1.91E-07	1.59E-03	6.03E-04	2.32E-03	2.78E-07	1.59E-03	2.44E-03	9.39E-03	7.28E-07	6.07E-03	2.30E-03	8.85E-03	9.84E-07	6.07E-03
S17	6.52E-04	2.57E-03	3.35E-07	7.15E-03	6.69E-04	2.53E-03	2.70E-07	4.58E-03	2.67E-03	9.82E-03	1.28E-06	2.73E-02	2.55E-03	9.67E-03	1.03E-06	1.75E-02
S18	6.04E-04	2.75E-03	3.61E-07	3.22E-02	6.89E-04	2.91E-03	3.35E-07	1.84E-02	2.49E-03	1.05E-02	1.38E-06	1.23E-01	2.63E-03	1.11E-02	1.28E-06	7.03E-02
S19	5.73E-04	2.29E-03	3.61E-07	1.66E-03	5.92E-04	2.25E-03	3.61E-07	1.66E-03	2.31E-03	8.76E-03	1.38E-06	6.35E-03	2.26E-03	8.59E-03	1.38E-06	6.35E-03
S20	6.06E-04	2.11E-03	BDL	1.66E-03	1.19E-04	1.99E-03	BDL	1.66E-03	2.19E-03	8.07E-03	BDL	6.35E-03	4.54E-03	7.61E-03	BDL	6.35E-03
S21	5.81E-04	1.90E-03	BDL	BDL	6.91E-04	2.33E-03	4.12E-07	1.55E-03	2.31E-03	7.24E-03	BDL	BDL	2.64E-03	8.88E-03	1.57E-06	5.93E-03
S22	6.57E-04	2.12E-03	BDL	1.85E-03	6.03E-04	2.27E-03	4.12E-07	1.85E-03	2.22E-03	8.09E-03	BDL	7.06E-03	2.30E-03	8.66E-03	1.57E-06	7.06E-03
S23	6.77E-04	2.42E-03	3.09E-07	1.89E-03	6.76E-04	2.48E-03	3.22E-07	1.92E-03	2.51E-03	9.23E-03	1.18E-06	7.20E-03	2.58E-03	9.45E-03	1.23E-06	7.34E-03
S24	7.31E-04	2.43E-03	4.12E-07	2.48E-03	6.73E-04	2.37E-03	3.61E-07	2.48E-03	2.59E-03	9.28E-03	1.57E-06	9.46E-03	2.58E-03	9.03E-03	1.38E-06	9.46E-03
S25	6.15E-04	2.82E-03	3.86E-07	1.53E-03	6.81E-04	2.63E-03	3.74E-07	2.40E-03	2.79E-03	1.08E-02	1.48E-06	5.86E-03	2.60E-03	1.00E-02	1.43E-06	9.18E-03
S26	6.37E-04	2.68E-03	3.61E-07	BDL	6.48E-04	2.61E-03	4.12E-07	1.48E-03	2.35E-03	1.02E-02	1.38E-06	BDL	2.47E-03	1.02E-02	1.57E-06	5.65E-03
S27	6.51E-04	2.31E-03	BDL	1.63E-03	6.65E-04	2.49E-03	4.12E-07	1.57E-03	2.43E-03	8.82E-03	BDL	6.21E-03	2.53E-03	9.52E-03	1.57E-06	6.00E-03
S28	5.25E-04	2.46E-03	BDL	2.99E-03	6.41E-04	2.45E-03	3.35E-07	2.99E-03	2.48E-03	9.38E-03	BDL	1.14E-02	2.45E-03	9.35E-03	1.28E-06	1.14E-02
S29	5.54E-04	1.94E-03	BDL	BDL	6.61E-04	2.51E-03	3.61E-07	1.85E-03	2.00E-03	7.42E-03	BDL	BDL	2.55E-03	9.58E-03	1.38E-06	7.06E-03
S30	5.20E-04	2.19E-03	BDL	1.52E-03	5.33E-04	2.08E-03	3.61E-07	1.53E-03	2.12E-03	8.37E-03	BDL	5.79E-03	2.01E-03	7.93E-03	1.38E-06	5.86E-03
S31	6.57E-04	2.13E-03	3.61E-07	1.57E-03	5.98E-04	2.40E-03	3.74E-07	1.66E-03	1.99E-03	8.15E-03	1.38E-06	6.00E-03	2.28E-03	9.15E-03	1.43E-06	6.35E-03
S32	5.71E-04	2.28E-03	3.09E-07	BDL	6.87E-04	2.50E-03	3.35E-07	1.44E-03	2.51E-03	8.70E-03	1.18E-06	BDL	2.62E-03	9.55E-03	1.28E-06	5.51E-03

S33	6.59E-04	2.12E-03	BDL	BDL	6.96E-07	2.65E-03	3.61E-07	1.74E-03
S34	4.86E-04	2.29E-03	3.61E-07	1.63E-03	7.72E-04	2.75E-03	3.48E-07	1.87E-03
S35	6.82E-04	1.83E-03	BDL	BDL	5.25E-04	1.93E-03	BDL	1.59E-03
S36	7.32E-04	2.50E-03	3.35E-07	2.22E-03	7.13E-04	2.61E-03	3.86E-07	2.22E-03
S37	7.31E-04	2.85E-03	3.61E-07	2.00E-03	6.51E-04	2.54E-03	3.61E-07	2.00E-03
S38	6.87E-04	2.64E-03	3.09E-07	1.96E-03	7.71E-04	2.62E-03	3.09E-07	2.81E-03
S39	6.24E-04	2.38E-03	3.09E-07	1.81E-03	7.46E-04	2.55E-03	3.09E-07	9.24E-04
S40	6.26E-04	2.34E-03	3.09E-07	2.54E-02	6.78E-04	2.62E-03	3.22E-07	1.34E-02
S41	6.26E-04	2.33E-03	3.09E-07	1.48E-03	7.28E-04	2.67E-03	3.35E-07	1.89E-03

2.18E-03	8.08E-03	BDL	BDL	2.66E-03	1.01E-02	1.38E-06	6.64E-03
2.52E-03	8.73E-03	1.38E-06	6.21E-03	2.94E-03	1.05E-02	1.33E-06	7.13E-03
1.86E-03	7.00E-03	BDL	BDL	2.00E-03	7.37E-03	BDL	6.07E-03
2.60E-03	9.54E-03	1.28E-06	8.47E-03	2.72E-03	9.96E-03	1.48E-06	8.47E-03
2.79E-03	1.09E-02	1.38E-06	7.62E-03	2.48E-03	9.71E-03	1.38E-06	7.62E-03
2.79E-03	1.01E-02	1.18E-06	7.48E-03	2.94E-03	1.00E-02	1.18E-06	1.08E-02
2.62E-03	9.07E-03	1.18E-06	6.92E-03	1.22E-01	9.75E-03	1.18E-06	3.53E-03
2.38E-03	8.94E-03	1.18E-06	9.68E-02	2.59E-03	1.00E-02	1.23E-06	5.12E-02
2.39E-03	8.90E-03	1.18E-06	5.65E-03	2.78E-03	1.02E-02	1.28E-06	7.20E-03

## 4.7 Microbial Parameters

### 4.7.1 *Escherichia Coli* (*E. coli*)

According to the WHO guidelines for drinking water quality (WHO, 2011), there must be no detectable concentration of *E. coli* in (0 cfu/100 ml) in water from any source. The level of *E. coli* in the studied springs ranged from 0 - 6 cfu/100 ml in the dry season, with a mean of  $0.370 \pm 0.02$  and 0 – 7.66 cfu/100 ml in the wet season with a mean of  $0.881 \pm 0.34$  cfu/100 ml. The results showed that 65.85% and 41.46% of samples in the wet and the dry seasons fell within the standard limit and complied with WHO drinking water and domestic use standard guideline of 0 cfu/100 ml (Table 4.12). Other sampled spring water was not suitable for drinking purposes, however, 78.04% (dry) and 65.85% (wet) complied with the levels for agriculture and recreation purposes of (1 cfu/100 ml) (WHO, 2011). Exposure to spring water associated with *E. coli* can cause diseases such as diarrhoea and cholera.

There was a strong correlation between *E. coli* and *Faecal coliform* that was detected ( $r = 0.52$  on dry) and ( $r = 0.62$  on wet) (Appendix 5 and 6). This is because the presence of *E. coli* in spring water indicates a faecal contamination, which is an extreme health hazard. The trace of coliform in spring water also shows environmental contamination; this can be associated with potential ill-health effects such as, diarrhoea, stomach pains, nausea and fever. In this study, the p values showed no statistical difference between the studied seasons of the *E.coli* mean of ( $P > 0.05$ ) (Appendix 2). Enitan-Folami et al. (2018) recorded *E. coli* results which also exceeded the standard limit of WHO with a range of ( $2.0 \times 10^1 - 4.6 \times 10^3$  CFU/100 ml) wet and ( $0.0 - 7.0 \times 10^2$  CFU/100 ml) for dry Thulamela Municipality, South Africa; this is higher than the ones recorded in this study. The spatial distribution map of *E. coli* in (Figure 4.36) shows higher levels in the wet seasons compared to the dry seasons. Another Study by Odiyo et al. (2020) recorded high level of *E.coli*, compared to this study and exceeded the standard regulations of (WHO, 2011)

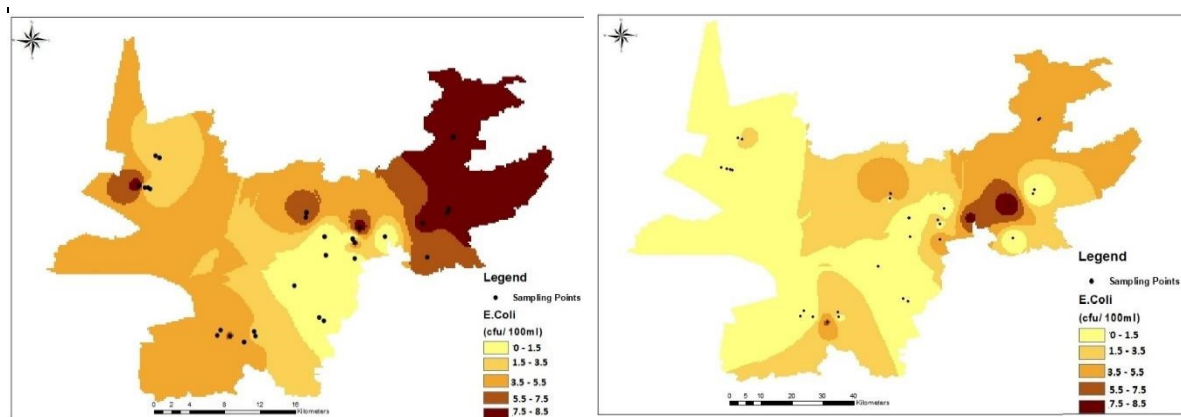


Figure 4.36: Spatial Distribution of *E. coli* (A- wet season and B- dry season)

Table 4.12: Average and standard deviation of microbial of the studied parameters in spring water

	Total Coliform (cfu/ 100mL)		Faecal Coliform(cfu/ 100mL)		E. coli (cfu/ 100mL)	
	Dry	Wet	Dry	Wet	Dry	Wet
S1	322.33±257.17	759.67±291.03	9±0.57	9.33±0.62	0±0	0.33±0.51
S2	177.33±72.16	573.33±86.22	7.33±0.57	10.33±0.29	1±0.61	2±0.72
S3	220.67±75.47	766.33±77.66	0±0	0.56±0.96	0±0	0±0
S4	216±20.8	838.67±37.85	0±0	6.33±0.45	0±0	0±0
S5	240.333±146.83	559.667±242.44	6.667±0.11	6.33±0.45	1.33±0.73	1.8±0.21
S6	266.667±141.33	852.33±293.77	1.33±0.33	4.333±2.5	0±0	3.33±0.96
S7	326.667±110.11	598.33±231.88	6.33±0.92	14.67±7.09	0±0	2.33±0.65
S8	188.667±84.33	264.33±72.92	3±0.13	4.33±0.19	0±0	1±0.04
S9	217.333±180.66	894.33±251.91	6.33±3.4	2±0.5	1.33±0.16	0±0
S10	194±188.07	592.67±423.75	1.33±0.36	17.66±1.15	0±0	0±0
S11	509.33±159.81	1229±826.01	2.67±1.5	7.333±2.3	0±0	1.33±0.84
S12	430±243.28	1015±267.22	15.331.2±	14±1.63	0.33±0.04	0.33±0.91
S13	434.33±401.76	2052±169.71	0.33±0.7	7.33±0.23	0±0	2.33±0.34
S14	485.5±123.06	991.33±889.48	5.33±0.37	5.667±1.38	0.33±0.05	1±0.85
S15	440.33±391.32	1699.333±112.50	3.33±0.5	4.333±0.11	0.2±0.07	0.33±0.08
S16	348±336.61	1021.6667±354.22	3.333±2.01	2.67±0.75	0±0	0.33±0.02
S17	361.33±293.44	1369±61.5	8±1.5	1.33±0.33	0±0	0±0
S18	272.33±226.56	1331±636.67	5.672.08±	1.667±0.24	0±0	0±0
S19	202.33±200.78	577±270.36	2.667±1.15	0.667±0.41	0±0	0±0
S20	244±19.28	1214±356.66	5±1.45	13.33±4.5	1±	1.667±0.32
S21	327±311.12	1599.33±378.16	4±2.4	2.667±0.92	0±0	0±0
S22	356.67±351.97	1987.3±112.16	0±0	0.667±0.02	0±0	0±0
S23	469±329.59	1169.667±830.69	3.67±0.22	3.67±0.35	0±0	0.667±0.43
S24	336±310.04	1484.667±327.95	17.33±1.96	6.33±0.13	6±1.6	7.667±9.2
S25	184.33±116.51	861±551.87	7.3±1.6	2.67±0.02	0.33±0.03	1.333±0.27
S26	154±135.23	1072±152.43	17.33±4.2	12.33±4.5	2±0.79	1.333±0.23
S27	173±153.52	1030±179.03	4.67±0.37	3.33±1.033	0±0	0.33±0.05
S28	313±91.42	1515.33±902.9	3.33±0.57	0.33±0.07	0.33±0.75	0±0
S29	400±67.02	1298.67±706.33	0.3±0.011	0.667±0.19	0±0	0±0
S30	220.33±163.13	1020.66±694.17	8.33±3.3	5.33±4.40	0±0	1.66±0.78

S31	344±117.93	1712.67±690.25	7.92±4.6	8.67±1.93	0.33±0.82	2.33±0.67
S32	294.66±161.68	937.33±24.95	0.667±0.43	1±0.43	0±0	0±0
S33	260.33±207.76	808±231.66	0±0	5±0.94	0±0	1.33±0.032
S34	367.66±354.56	1534.33±482.75	3.33±1.06	5.33±0.73	1.33±0.56	2.67±0.28
S35	454±224.14	1781.667±99.51	0.33±1.02	3.67±0.86	0±0	5.67±0.59
S36	317±238.49	1178.33±430.77	0±0	0±0	0±0	0±0
S37	204±150.19	1224±552.73	2±0.35	3.33±0.03	0±0	0±0
S38	410.33±357.5	1566.33±785.62	0.7±0.02	1±0.64	0±0	0±0
S39	257±222.5	993.667±440.02	1.667±0.67	2.33±0.06	0±0	0±0
S40	100±63.69	1005±190.49	3.667±0.89	7.33±1.4	0.33±0.08	1±0.34
S41	159±110.81	1002.67±183.15	0±0	0±0	0±0	0±0

#### 4.7.2 Faecal Coliform

Faecal coliforms are crucial parameters to consider when evaluating the suitability of drinking water due to their potential to cause diseases that are infectious. *Faecal coliform* has 0 cfu/100ml tolerance in drinking water (WHO, 2011). Concentration of *Faecal coliforms* ranged from 0 -17.67 cfu/100 ml in the (dry season) and 0 -17.83 cfu/100 ml in the (wet season) with averages of  $4.380 \pm 2.9729$  cfu/100 ml and  $5.0947 \pm 4.19$  cfu/100 ml respectively (Table 4.12). The spring which recorded the highest concentration of *faecal coliform* was S26; it is located at a low level near where agriculture is practiced and faeces are carried into the spring water during runoffs. Faecal coliform in water is associated with illnesses and diseases; these include hepatitis, typhoid fever and gastroenteritis (Aram et al., 2021). In each observed period, 14.6% (dry) and 4.87 % (wet), the springs complied with the standard limit of WHO (0 cfu/100ml), while 85.4% and 95.13% did not comply (Table 4.12). This can be clarified by the fact that these springs are found not far from houses utilizing individual septic tanks. Spring water quality was poor overall, in relation to *faecal coliform*, with over 80% in both seasons failing to meet any of the criteria set by WHO (2011).

The results recorded in the study showed that the mean of faecal levels of the samples was significantly different ( $P < 0.05$ ) between the wet and the dry season. Spatial distribution of faecal coliform was found to be high in north-eastern (wet) and south-eastern parts (dry season) of Thulamela Municipality (Figure 4.37). *Faecal coliform* in spring water is usually from domestic sewages, waste from animals and non-point sources. A study conducted by Enitan-Folami et al. (2018) recorded high concentrations with a value for *total* faecal coliform of  $2.0 \times 10^0 - 6.0 \times 10^2$  CFU/100 ml) wet and  $0.0 - 1.0 \times 10^1$  CFU/100 ml dry.



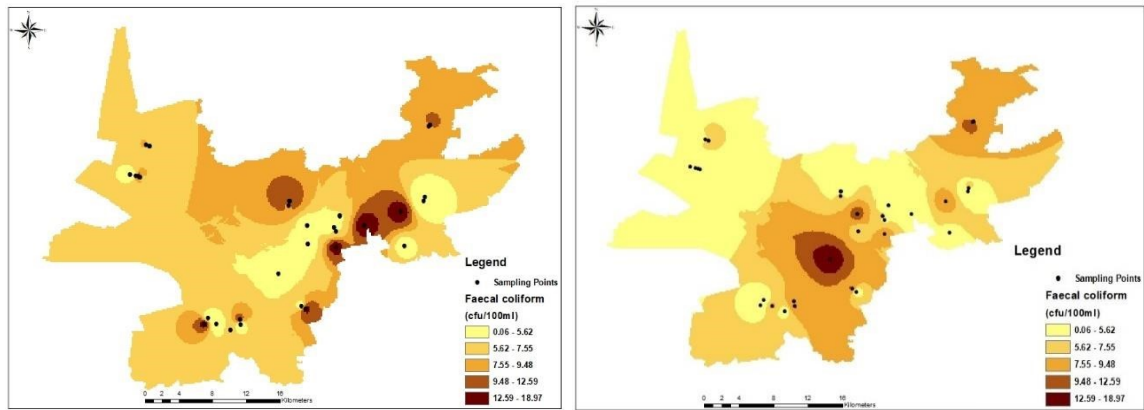


Figure 4.37: Spatial Distribution of Faecal coliform (A- wet season and B- dry season)

#### 4.7.3 Total Coliform (TC)

As presented in Table 4.12, most of the spring water samples, in Thulamela Municipality contained high values of total coliforms. Total coliforms were detected in all of the springs' sampling points for both dry and wet seasons with an average of 173 - 509.33 cfu/100 ml and 808- 1987.33 cfu/100 mL, respectively, with an average of  $297.53 \pm 104.073$  (dry) and  $1121.50 \pm 410.98$  (wet) (Table 4.12). 100% of both studied seasons at Thulamela Municipality showed presence of total coliform in the spring water. This may be attributed to the constructions around the area, runoff water, sewage and the faeces of humans and animals. *Total coliform* values recorded were above the recommended level for drinking water at 10 cfu/100ml (WHO, 2011).

Total coliforms include bacteria that are found in spring water, and although they are not harmful, spring water samples containing them indicate pollution (Appendix 7). The results recorded in the study showed significant difference in the concentration of total coliform during the dry and the wet seasons ( $P < 0.05$ ). A similar study was conducted by Luvhimbi et al. (2022) at Thulamela municipality, Limpopo Province revealed that coliforms were also significantly present at high level. The spatial distribution map of total coliform (Figure 4.38) shows dissimilar trends in wet and dry seasons.

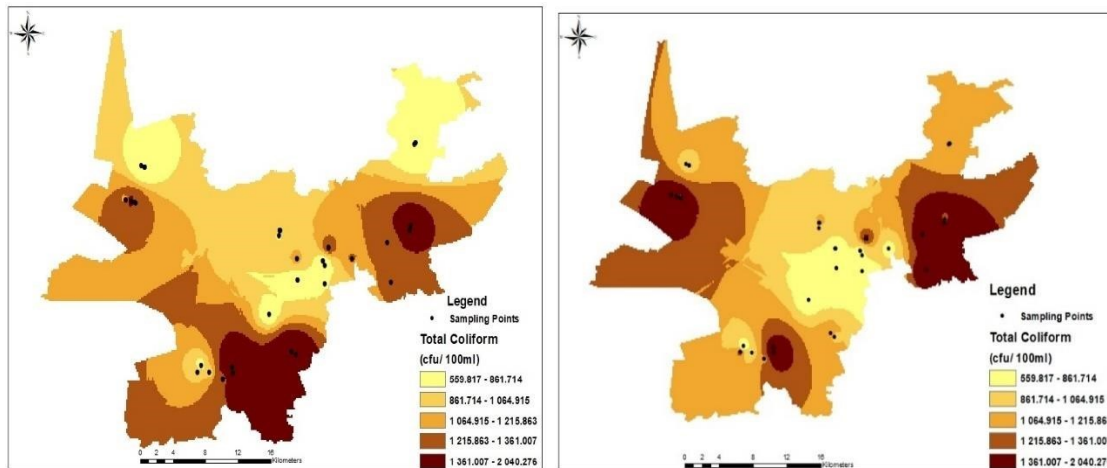


Figure 4.38: Spatial Distribution of Total coliform (A- wet season and B- dry season)

#### 4.8 Quantitative Microbiological Risk Assessment (QMRA)

*E. coli* are often used in QMRA studies to present the risk associated with the consumption of microbial-contaminated water (Kundu et al., 2018, Haas, 1999). In this study, this parameter was one of the microbial parameter studied to show the risks associated with contamination of spring water. The average ingested dose of *E. coli* (cfu/day) for dry and wet season of spring water showed a ranged of (0–0.48 cfu/day) (dry) and (0- 0.613) (wet) as presented in (Table 4.13).

*E. coli* is one of the commonly used reference/pathogen in QMRA. The risk of infections, per day in percentages, was computed for dry and wet seasons. For children was recorded 0–2.38 (dry) and 0- 2.936 (wet) with a mean of  $0.170195 \pm 0.4159\%$  (dry) and  $0.459 \pm 0.639\%$  (wet) (Table 4.13). The results for the children showed 36.58% (dry) and 65.85% (wet) chances of infection per day with *E. coli*. Adults recorded higher risk of infection as compared with children with a range of 0- 26.56% (dry) and 0 - 27.46 (wet) with averages of  $6.24 \pm 9.04\%$  (dry) and  $12.10 \pm 10.64\%$  (wet) (Table 4.13). This can be due to the fact that adults use spring water more for various activities, such as washing clothes, drinking and agriculture, and that increases the chances of infection. The risks of infection per day in (%) recorded for *E. coli* pathogen was relative with maximum value observed at S24 for both child and adult at 2.38% (dry); 2.93% (wet) for child and 26.56% (dry); 27.45% (wet) for adults (Table 4.13).

The annual risk of infection was relatively high as observed in this study with highest values of 99.58% (child) and 98.80% (adult) (Table 4.13). Water from S24 showed the highest risk of

annual infections (Table 4.13). The risk of illness values showed a range of 0-34.86% (adult) and 0-35% (child) of illness per year for *E. coli*, with maximum values found at S24 (Table 4.13).

Table 4.13: *E. coli* dose ingested; risk of infection per day; risk of illness and infection per year

	Average Ingested dose of <i>E.coli</i> (CFU/day)		Risk of Infection per day for child (%)		Risk of Infection per day for Adult (%)		Risk of illness per year (%)		Risk of infection per year (%)	
	<i>Dry</i>	<i>Wet</i>	<i>Dry</i>	<i>Wet</i>	<i>Dry</i>	<i>Wet</i>	<i>Adult</i>	<i>Child</i>	<i>Adult</i>	<i>Child</i>
Springwater	<i>Dry</i>	<i>Wet</i>	<i>Dry</i>	<i>Wet</i>	<i>Dry</i>	<i>Wet</i>	<i>Adult</i>	<i>Child</i>	<i>Adult</i>	<i>Child</i>
S1	0	0.03	0	0.15	0	15.29	5.09	27.66	12.56	14.53
S2	0.08	0.16	0.45	0.88	19.73	22.44	26.06	35.00	68.31	74.46
S3	0	0	0	0	0	0	0	0	0	0
S4	0	0	0	0	0	0	0	0	0	0
S5	0.11	0.14	0.60	0.80	20.86	22.03	26.57	35.00	69.80	75.90
S6	0	0.27	0	1.42	0	24.38	27.27	35.00	71.89	77.91
S7	0	0.19	0	1.02	0	23.03	23.01	34.99	59.54	65.73
S8	0	0.08	0	0.45	0	19.73	13.06	34.43	32.81	37.32
S9	0.12	0	0.59	0	20.86	0	16.17	34.80	40.96	46.21
S10	0	0	0	0	0	0	0	0	0	0
S11	0	0.11	0	0.59	0	20.86	16.17	34.80	40.96	46.21
S12	0.02	0.03	0.15	0.15	15.26	15.29	9.36	33.08	23.31	26.74
S13	0	0.18	0	1.01	0	23.03	23.01	34.99	59.54	65.73
S14	0.02	0.08	0.15	0.45	15.25	19.73	16.15	34.80	40.88	46.13
S15	0.02	0.03	0.09	0.15	13.20	15.30	7.76	31.82	19.27	22.18
S16	0	0.03	0	0.15	0	15.30	5.09	27.67	12.57	14.54
S17	0	0	0	0	0	0	0	0	0	0
S18	0	0	0	0	0	0	0	0	0	0
S19	0	0	0	0	0	0	0	0	0	0
S20	0.08	0.13	0.45	0.74	19.73	21.73	24.65	34.99	64.22	70.43
S21	0	0	0	0	0	0	0	0	0	0
S22	0	0	0	0	0	0	0	0	0	0
S23	0	0.05	0	0.35	0	18.11	9.40	33.11	23.42	26.87
S24	0.48	0.61	2.38	2.94	26.57	27.46	34.86	35.00	98.80	99.59

S25	0.02	0.11	0.15	0.60	15.26	20.86	18.80	34.92	47.96	53.71
S26	0.16	0.11	0.88	0.60	22.44	20.86	27.27	35.00	71.89	77.91
S27	0	0.02	0	0.15	0	15.26	5.04	27.56	12.45	14.41
S28	0.02	0	0.15	0	15.26	0	5.04	27.56	12.45	14.41
S29	0	0	0	0	0	0	0	0	0	0
S30	0	0.13	0	0.74	0	21.73	18.82	34.93	48.03	53.78
S31	0.02	0.18	0.15	1.01	15.29	23.03	24.65	34.99	64.21	70.43
S32	0	0	0	0	0	0	0	0	0	0
S33	0	0.10	0	0.59	0	20.86	16.17	34.8	40.95	46.213
S34	0.10	0.21	0.60	1.15	20.85	23.54	29.19	35.00	77.77	83.39
S35	0	0.45	0	2.27	0.00	26.36	32.11	35.00	87.40	91.73
S36	0	0	0	0	0	0	0	0	0	0
S37	0	0	0	0	0	0	0	0	0	0
S38	0	0	0	0	0	0	0	0	0	0
S39	0	0	0	0	0	0	0	0	0	0
S40	0.03	0.08	0.15	0.45	15.26	19.73	16.15	34.80	40.88	46.13
S41	0	0	0	0	0	0	0	0	0	0

The presence of *E.coli* pathogen in water can lead to extremely high health problems, if the water is ingested. The study findings revealed a high prevalence of *E. coli* risk in the wet season compared to the dry season (Table 4.13). The WHO (2011) standard guideline is (0 cfu/100 ml) which is acceptable for drinking purposes. These results showed that some of the spring water did not comply with the recommended level. This indicates that chances of diseases from *E. coli* may be associated with Thulamela Municipality.

Results obtained by Taonameso et al., (2020) showed that 31 (25%) of 125 (100%) chosen sampling points at Vhembe District were capable of causing risk to human health. This is as recommended by WHO (2011) that there should not be any trace of *E. coli* in water. This study discovered counts of *E. coli* that were greater than 10 cfu/100 mL in some sampling sites. Similarly, another study by Odiyo et al., (2020) at Vhuronga 1 Limpopo Province showed a range of 34.9–35% *E.coli* which can lead to illnesses. The results of this study can also be compared to other studies conducted by Ahmed et al., (2020); Palamuleni et al. (2018) and Mpenyana-Monyatsi et al. (2017)

## CHAPTER 5: CONCLUSION AND RECOMMENDATION

### 5.1 Conclusion

The aim of this study was to evaluate water quality, geochemistry process, and health risks associated with spring water in Thulamela Municipality. Most of the physical parameters (pH, TDS, EC, salinity, temperature, and turbidity) complied with the limit set by (SANS, 2015 and WHO, 2011) except for turbidity in a few selected sites of the dry season (15) and 41 sites in the wet season. Total coliform was recorded in all of the samples, in both seasons. *Faecal coliform* showed 85.4% and 95.13% presence in the dry and wet season, respectively. Whereas *E. coli* was detected in 34.15% (dry) and 58.53% (wet) of the samples. The wet season recorded high microbiological presence, compared to the dry season. Most of the trace elements tested (Al, V, Mn, Fe, Co, Ni, Cu, Zn, Cr, As, Se, Sr, Mo, Cd, Sn, Sb, Ba, Hg, Pb, and Si), complied with the threshold limit except for Sb in the wet season. The major cations tested in the study (Na, Mg, P, K, and Ca) fell within WHO and SANS permissible limits in both studied seasons. The major anions (fluoride, chloride, nitrite, nitrate, bromide, phosphate, and sulphate) complied with the regulatory limit except for Nitrate, Bromide, and Phosphate.

The WQI computed based on the physicochemical and trace metals levels showed that all the spring can be regarded as excellent water with good quality in the dry season and 80% of the samples in the wet season. However, with the inclusion of microbiological parameters most of the springs can be regarded as having poor water quality. The result of the present study indicated that all of the metals were not capable, individually, of posing any adverse health effect, through ingestion or dermal contact, on children and adults as the hazard quotient and hazard index values were less than one.

The major types of water found in this study were Ca-Mg-Cl, Ca-Cl and Ca-HCO<sub>3</sub> which are gypsum ground water, water from mine drainage and shallow levels; the ion-exchange process was from the influence of fresh ground water. However, the dominant water type in were Ca-MgCl and Ca-HCO<sub>3</sub> in the wet and dry seasons respectively. The principal hydrochemical process shaping the ground water chemistry was dilution or mixing.

Quantitative Microbiological Risk assessment (QMRA) results obtained in this study showed the risks of infection per day were relatively low in dry and wet seasons; for children it was recorded at 0-2.38% (dry) and 0- 2.936% (wet); adults recorded higher risk of infection with a range of 0- 26.57% (dry) and 0- 27.46% (wet). There was a relatively high annual risk of

infections observed in this study with the highest values of 99.58% (child) and 98.80% (adult). There is a need for management plans for the Thulamela Municipality's water springs to avoid the progression of waterborne diseases in the communities that consume spring water.

## 5.2 Recommendations

1. Spring protection mechanisms should be designed and tested for efficiency.
2. There should be constant monitoring of spring water quality in the local municipality.
3. The point-of-use water treatment devices should be utilised by communities who rely on spring water, to deter any possible health risk.

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## APPENDICES

### Appendix 1: Standard guidelines for domestic, agriculture and recreation purposes.

Parameters	Limit of Agriculture, recreation and domestic water use (WHO, 2011)				
	Livestock	irrigation	Aquaculture	Recreation	Domestic (human consumption)
Temperature (°C)	n/a	n/a	n/a	n/a	n/a
pH	n/a	6.5-8.4	6.5-9.0	6.5 - 8.5	6 - 9
Salinity (mg/L)	n/a	n/a	n/a	n/a	n/a
TDS (mg/L)	0-3000	n/a	n/a	n/a	0 - 450
Turbidity (NTU)	n/a	0 - 50	n/a	n/a	>1
Al (mg/L)	0 - 5	0 - 5	0-3	n/a	0 - 0.15
As (mg/L)	0 - 1	0 - 1	0-0.005	n/a	0 - 0.01
Beryllium (mg/L)	n/a	0 - 0.1	n/a	n/a	n/a
Boron (mg/L)	0 - 5	0 - 5	n/a	n/a	n/a
Cadmium (mg/L)	0 - 10	0 - 10	0 - 0.2	n/a	0 - 5
Calcium (mg/L)	0 - 1 000	n/a	n/a	n/a	0 - 32
Chloride (mg/L)	0 - 3 000	0 - 1.00	0 - 600	n/a	0 - 100
Chromium (mg/L)	0 - 1	0 - 1	0-0.02	n/a	0 - 0.05
Cobalt	0 - 1	0 - 0.05	n/a	n/a	n/a
E.coli (cfu/100ml)	n/a	n/a	n/a	0 - 130	0
Faecal Coliform (cfu/100ml)	0 - 200	<1	n/a	0 - 150	0
Total coliform (cfu/100ml)	n/a	n/a	n/a	n/a	0 - 5
Copper (mg/L)	0 - 5	0 - 0.2	0.005	n/a	0 - 1
Fluoride (mg/L)	0 - 2	0 - 2	n/a	n/a	0 - 1
Iron (mg/L)	0 - 10	0 - 5	0.01	n/a	0 - 0.1
Lead (mg/L)	0 - 0.1	0 - 0.2	0-0.01	n/a	0 - 0.01
Lithium (mg/L)	n/a	0 - 2.5	n/a	n/a	n/a
Magnesium (mg/L)	0- 500	n/a	n/a	n/a	0 - 30
Mercury (mg/L)	0 - 1.0	n/a	0 - 0.001	n/a	0 - 0.001
Molybdenum (mg/L)	0 - 0.01	0 - 0.01	n/a	n/a	n/a
Nickel (mg/L)	0 - 1	0 - 0.20	n/a	n/a	n/a
NO <sub>3</sub> <sup>-</sup> Nitrate (mg/L)	0 - 100	n/a	0 - 0.05	n/a	0 - 6
NO <sub>2</sub> <sup>-</sup> Nitrite	0 - 10	n/a	n/a	n/a	0 - 6

Phosphorus (mg/L)	n/a	n/a	0.1	n/a	n/a
Potassium (mg/L)	n/a	n/a	n/a	n/a	0 - 50
Selenium (mg/L)	0 - 50	0 - 0.02	0 - 0.3	n/a	0 - 0.02
Silica (mg/L)	n/a	n/a	n/a	n/a	n/a
Sodium (mg/L)	0 - 2 000	70	n/a	n/a	0 - 100
Sulphate (mg/L)	0 - 1000	n/a	n/a	n/a	0 - 200
Sulphides (mg/L)	n/a	n/a	0.001	n/a	n/a
Uranium (mg/L)	n/a	0 - 0.01	n/a	n/a	n/a
Vanadium (mg/L)	0 - 1	0 - 0.1	n/a	n/a	0 - 0.1
Zinc (mg/L)	0 - 20	0 - 1	0.03	n/a	0 - 3

**Appendix 2: Shows P values to present statistical variance between dry and wet season**

Parameters	P-values	Grade	Parameters	P-values	Grade
B (µg/L)	0.00250	Significant	Total coliform (cfu/100ml)	2.1E-20	Significant
Al (µg/L)	0.12097	Not Significant	Faecal coliform (cfu/100ml)	0.0021	Significant
V (µg/L)	0.4876	Not Significant	E. coli (cfu/100ml)	0.871	Not Significant
Co (µg/L)	0.1487	Not Significant	EC (mS/m)	0.220	Not Significant
Se (µg/L)	1.1487	Not Significant	Temperature	0.00071	Significant
Sr (µg/L)	2.1487	Not Significant	pH	3.04E-28	Significant
Sn (µg/L)	3.1487	Not Significant	Salinity (mg/L)	0.1018	Not Significant
Sb (µg/L)	0.9225	Not Significant	TDS (mg/L)	0.088	Not Significant
Hg (µg/L)	0.7310	Not Significant	Turbidity (NTU)	5.18E-09	Significant
Mn (µg/L)	0.05	Significant	F (mg/L)	0.888	Not Significant
Fe (µg/L)	0.083	Not Significant	Cl (mg/L)	0.431569	Not Significant
Ni (µg/L)	0.0004	Significant	SO <sub>4</sub> (mg/L)	0.936508	Not Significant
Cu (µg/L)	0.001	Significant	PO <sub>4</sub> (mg/L)	BDL	Significant
Zn (µg/L)	0.77516	Not Significant	NO <sub>2</sub> (mg/L)	BDL	Significant
Cr (µg/L)	0.00038	Significant	Br (mg/L)	0.445705	Not Significant
As (µg/L)	0.0497	Significant	NO <sub>3</sub> (mg/L)	0.080386	Not Significant
Mo (µg/L)	0.0078	Significant	Na (mg/L)	0.559262	Not Significant
Cd (µg/L)	0.0616	Not Significant	Mg (mg/L)	0.818025	Not Significant
Ba (µg/L)	0.233	Not Significant	Si (mg/L)	0.383357	Not Significant
Pb (µg/L)	0.1542	Not Significant	P (mg/L)	0.428465	Not Significant
Ca (mg/L)	0.4635	Not Significant	K (mg/L)	0.311062	Not Significant

p > 0.05 (Insignificant); p < 0.05 (significant)

**Appendix 3: Concentration of Trace elements and SD for Dry season**

Sample ID	B (µg/L)	Al(µg/L)	V (µg/L)	Mn (µg/L)	Fe (µg/L)	Co (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)	Cr (µg/L)	As (µg/L)	Se (µg/L)	Sr (µg/L)	Mo (µg/L)	Cd (µg/L)	Sn (µg/L)	Sb (µg/L)	Ba (µg/L)	Hg (µg/L)	Pb (µg/L)	Si (mg/L)
S1	14.3±2.72	100.665±67.58	2.185±0.32	15.04±7.47	314.485±141.20	0.835±0.06	18.39±2.91	5.635±1.42	11.675±3.64	38.19±5.80	0.07±0	BDL	35.545±5.65	0.74±0.18	0.065±0.48	17.215±23.62	0.48±0.62	11.11±5.16	0.04±0	0.47±0	22.93±7.81
S2	11.51±0.98	36.365±11.38	1.35±1.19	8.005±47.10	265.365±11.66	1.425±0.25	18.26±2.56	2.815±1.14	5.63±1.27	39.195±4.52	0.085±0.01	BDL	25.17±0.10	0.8±0.13	0.07±0	24.185±24.19	0.045±0.04	17.13±0.68	BDL	0.41±0	12.8±1.12
S3	8.755±2.30	63.795±16.94	1.35±0	8.005±2.67	259.48±42.82	0.6±0.03	15.155±2.73	2.935±1.69	6.14±2.55	32.07±5.18	0.07±0	BDL	25.605±1.36	0.63±0.16	BDL	37.82±21.55	0.04±0.01	17.13±2.09	BDL	BDL	16.26±2.69
S4	10.31±2.15	71.58±2.84	1.54±0.21	15.88±2.23	380.43±83.85	0.705±0.05	17.405±1.38	9.35±10.17	9.1±6.22	34.905±2.89	0.07±0	BDL	26.085±0.32	0.67±0.16	0.07±0	27.455±0.76	0.035±0.02	16.285±0.78	BDL	0.46±0	15.21±0.82
S5	9.24±4.58	126.665±31.49	0.72±0.25	15.355±7.57	554.79±156.81	1.23±0.33	21.62±2.01	6.355±0.91	9.17±2.98	43.675±4.07	0.07±0.01	BDL	56.77±4.20	0.765±0.06	0.065±0.01	31.21±3.11	0.055±0.04	83.225±7.35	BDL	0.47±0.01	9.04±1.48
S6	8.535±6.31	75.495±14.94	0.93±0.06	11.67±2.06	344.615±30.41	0.675±0.09	15.865±3.77	6.42±1.82	6.76±1.30	32.775±8.11	BDL	BDL	17.34±0.88	0.625±0.21	BDL	32.265±9.30	0.131±0.06	12.75±0.72	BDL	0.4±0	10.92±1.13
S7	7.05±4.10	91.3±52.95	1.12±0.51	9.84±5.37	268.07±96.62	0.67±0.14	16.9±0.45	5.515±0.84	8.15±0.96	34.955±0.93	0.07±0	BDL	18.38±0.06	0.64±0.03	0.06±0	32.605±0.23	0.045±0.01	13.185±0.62	BDL	0.46±0	11.805±1.05
S8	11.465±9.54	49.92±6.48	1.29±1.22	10.93±8.98	215.985±34.92	0.68±0.06	22.475±0.18	28.96±35.38	14.405±13.72	43.55±2.10	0.06±0	BDL	39.99±13.38	0.96±0.10	0.07±0	26.635±8.99	0.05±0	54.635±14.21	BDL	0.43±0.06	13.71±4.03
S9	7.48±6.84	39.265±7.08	0.48±0.04	13.845±11.18	152.86±52.12	0.485±0.02	16.1±0.04	4.42±1.27	7.73±4.88	30.76±2.57	0.075±0.01	BDL	39.13±8.92	0.595±0.05	0.06±0	29.13±4.53	0.05±0.01	57.52±11.23	BDL	2.62±0	11.405±1.45
S10	10±8.44	111.605±9.14	1.565±0.05	15.49±13.97	260.74±26.93	0.61±0.06	18.555±3.49	9.165±2.61	11.055±6.24	38.055±6.67	0.085±0.02	BDL	30.59±1.00	0.745±0.16	BDL	29.69±4.14	0.035±0.02	16.39±4.60	BDL	0.4±0.01	15.22±1.10
S11	9.215±2.67	217.585±109.86	5.235±1.24	9.865±3.51	517.305±178.88	0.795±0.08	19.36±3.69	4.07±0.95	4.79±0.04	41±7.59	0.115±0.04	BDL	35.265±0.18	0.76±0.24	BDL	13.215±17.50	0.885±1.22	4.88±0.62	0.09±0	0.54±0.16	20.035±2.58
S12	16.8±3.15	78.5±13.17	1.99±0.04	7.36±2.19	306.59±53.41	0.63±0.08	16.935±0.42	3.05±0.31	8.37±6.48	33.925±1.68	0.07±0	BDL	53.69±0.13	0.65±0.01	0.07±0	29.11±6.04	0.06±0.04	10.71±0.30	BDL	0.51±0	20.87±1.02
S13	5.535±4.04	77.895±18.83	1.575±0.16	14.29±3.71	232.655±51.63	0.72±0.14	18.78±0.03	3.145±0.78	4.755±0.54	34.46±0.28	0.1±0	BDL	66.53±1.34	0.72±0.01	0.06±0	32.855±7.23	0.035±0.01	39.43±3.42	BDL	BDL	15.63±1.68
S14	9.28±3.90	121.055±74.90	2.415±0.52	12.22±1.39	304.325±84.51	0.595±0.02	13.765±0.73	5.485±1.03	5.645±1.15	26.365±2.93	0.07±0	BDL	35.05±1.99	0.495±0.12	BDL	20.415±28.18	1.31±1.82	9.815±2.54	0.23±0	BDL	20.785±0.05
S15	9.89±0.76	63.345±51.60	1.75±0.24	73.18±78.53	446.24±597.58	0.89±0.82	9.1±11.05	2.53±0.17	7.19±5.18	18.995±24.73	0.075±0.21	BDL	39.945±7.23	0.76±0	BDL	24.895±5.62	0.045±0.01	12.53±2.42	BDL	0.41±0	20.675±2.11
S16	11.215±0.46	48.81±1.29	4.185±0.21	7.22±2.74	278.62±14.93	0.83±0.11	18.47±2.45	3.23±2.23	3.85±1.09	39.12±3.99	0.12±0.01	BDL	132.22±3.49	0.935±0.12	0.037±0	18.655±25.49	0.79±1.06	26.35±0.48	0.4±0	0.43±0	25.52±1.54
S17	12.445±4.82	128.27±75.29	5.725±1.18	11.78±0.40	563.705±179.26	0.925±0.05	20.25±1.70	37.125±48.35	6.01±1.95	40.915±2.41	0.135±0.02	BDL	154.015±13.97	1.055±0.16	0.065±0.01	30.075±1.45	0.045±0.02	34.07±2.28	BDL	1.935±2.11	29.52±5.64
S18	5.905±3.66	121.195±43.07	4.47±0.23	8.55±0.79	273.7±53.32	0.67±0.07	18.885±2.68	32.105±40.60	5.24±0.55	43.675±5.92	0.115±0.01	BDL	111.195±0.10	0.815±0.12	0.07±0	27.265±2.37	0.035±0.01	60.965±0.73	BDL	8.715±11.77	17.05±0.96
S19	9.515±4.35	57.255±23.65	2.06±0.04	3.985±1.10	178.975±56.90	0.57±0.20	17.485±4.32	4.14±2.19	5.01±2.19	36.48±8.27	0.12±0	BDL	74.035±3.44	0.755±0.15	0.07±0	14.73±19.50	0.585±0.78	55.7±3.58	0.4±0	0.45±0	16.275±1.83
S20	10.355±6.54	49.71±12.80	2.74±0.04	175.48±148.62	258.32±41.75	1.27±0.38	16.595±0.64	5.86±5.87	7.545±5.35	33.625±3.25	0.08±0	BDL	66.715±0.86	0.705±0.02	BDL	17.945±24.52	0.655±0.88	14.46±0.48	0.33±0	0.45±0	24.25±0.23
S21	43.09±0.98	51.635±16.00	13.935±0.09	103.62±20.87	181.82±13.38	2.37±0.59	17.55±0.71	16.3±14.86	13.865±8.46	30.17±1.58	0.135±0.06	0.605±0.01	182.665±5.06	1.285±0.16	BDL	19.63±24.99	0.7±0.93	24.17±0.68	0.29±0	BDL	32.91±1.39

S22	16.46±0.11	60.875±33.03	2.775±0.39	223.415±95.41	512.08±84.78	1.3±0.37	16.825±1.03	6.44±1.84	9.645±3.34	33.705±2.21	0.095±	BDL	84.155±0.57	0.695±0.08	BDL	33.355±7.39	0.07±0.06	21.665±0.06	0.02±0	0.5±0	19.185±0.69
S23	11.945±5.49	91.185±56.31	3.715±0.13	19.34±3.42	217.63±18.70	0.885±0.11	19.025±4.66	4.425±3.09	6.29±3.49	38.475±10.76	0.0467±0	BDL	87.65±1.87	0.78±0.18	0.06±0	29.96±2.01	0.04±0.01	5.83±0.27	BDL	0.51±0	27.755±0.63
S24	16.905±9.99	76.935±19.31	7.265±0.73	10.88±5.84	284.64±49.09	0.85±0.141	19.615±3.44	4.815±0.42	5.51±2.62	38.685±6.78	0.06±0	BDL	53.06±1.36	0.815±0.16	0.08±0	27.5±3.93	0.045±0.02	6.47±1.57	BDL	0.67±0.31	25.825±2.02
S25	17.65±7.42	80.71±6.07	2.085±0.11	16.635±2.71	297.295±82.80	0.89±0.28	21.18±4.82	4.76±0.23	7.905±0.80	44.795±9.00	0.085±0.01	BDL	25.195±3.32	0.845±0.18	0.075±0	30.185±3.25	0.05±0.03	10.97±0.74	BDL	0.415±0.04	24.045±3.17
S26	17.55±7.49	73.61±48.68	2.485±0.18	16.65±0.46	302.37±33.14	0.885±0.01	17.805±2.72	3.91±0.25	6.735±0.23	42.68±12.54	0.06±0	BDL	34.645±0.53	0.78±0.21	0.07±0	32.06±1.57	0.04±0.01	15.605±0.33	BDL	BDL	27.375±4.66
S27	9.8±9.89	77.21±5.63	1.775±0.65	12.85±0.5	297.875±135.73	0.73±0.10	18.435±2.06	7.625±4.71	11.365±7.97	36.75±0.11	0.09±0.03	BDL	25.875±7.93	0.7±0	BDL	29.86±8.02	0.125±0.12	12.66±4.34	0.01±0	0.44±0	17.91±7.89
S28	9.8±8.99	492.15±341.4	4.02±2.31	40.765±31.87	1017.145±606.66	2.01±1.37	18.84±1.92	16.26±13.28	6.69±1.41	39.08±3.45	0.09±0	BDL	19.415±1.61	0.51±0.14	BDL	24.975±5.78	0.03±0.01	14.48±1.60	BDL	0.81±0.34	12.53±1.97
S29	9.95±0.21	73.29±27.12	0.93±0.18	4.855±0.52	179.91±19.80	0.495±0.03	15.2±2.76	3.775±0.67	4.955±0.59	30.93±4.88	BDL	BDL	20.755±0.63	0.6±0.10	BDL	24.405±4.63	0.035±0.01	14.76±0.68	BDL	BDL	12.49±0.55
S30	10.15±0.99	297.435±191.21	1.845±1.68	21.085±20.99	892.13±482.72	1.18±0.76	16.055±4.41	20.31±20.53	6.475±0.78	34.855±8.11	BDL	BDL	8.2±2.73	0.58±0.30	BDL	31.225±8.08	0.05±0.03	9.13±0.54	BDL	0.41±0	4.85±0.04
S31	10.805±0.69	400.975±243.48	3.42±2.16	21.99±6.56	892.13±636.09	1.01±0.03	15.06±2.91	6.52±1.68	6.405±0.23	33.96±5.23	0.105±0.04	BDL	6.915±2.06	0.64±0.27	0.07±0	38.21±3.31	0.075±0.04	9±1.12	BDL	0.425±0.01	4.865±0.42
S32	8.365±2.06	97.32±12.53	0.5±0.01	26.68±6.94	298.62±23.26	1.12±0.13	19.015±4.28	4.05±0.74	6.88±0.49	36.255±9.95	BDL	BDL	5.215±0.59	0.665±0.19	0.06±0	25.35±3.87	0.045±0.01	7.43±0.22	BDL	BDL	3.23±0.14
S33	7.54±2.39	125.205±4.43	0.955±0.23	7.265±0.53	233.11±11.71	0.735±0.15	16.53±1.09	4.29±1.03	5.015±0.74	33.655±0.91	BDL	BDL	10.01±6.29	0.625±0.02	BDL	26.215±1.25	0.04±0	9.385±5.15	BDL	BDL	4.805±0.90
S34	23.94±2.02	60.445±4.80	0.99±0.14	4.065±0.53	186.2±47.31	1.205±0.15	19.085±5.03	3.82±2.66	6.47±2.11	36.365±9.10	BDL	BDL	26.495±3.42	0.705±0.21	0.07±0	26.955±4.12	0.07±0	13.895±1.42	BDL	0.44±0	12.98±0.62
S35	16.95±3.93	312.49±85.21	2.84±0.48	8.405±1.90	222.89±61.89	0.495±0.02	14.08±0.03	4.8±1.57	4.395±1.39	29.18±0.96	BDL	BDL	11.44±0.11	0.545±0.01	BDL	29.02±6.79	0.03±0.01	7.795±0.42	0.01±0	BDL	6.505±0.56
S36	17.44±3.30	287.805±48.47	2.635±0.18	11.905±0.30	263.015±34.34	0.68±0.01	19.74±0.06	7.7±2.56	9.445±0.49	39.77±0.20	BDL	BDL	11.4±0.06	0.785±0.04	0.065±0	24.26±1.82	0.035±0.01	7.36±0.17	BDL	0.6±0.25	6.14±0.57
S37	26.285±4.96	68.14±23.77	8.835±0.13	10.865±1.03	456.73±35.41	1.065±0.09	21.195±2.21	3.93±2.52	6.235±1.14	45.395±3.91	0.3±0.3	0.25±0.06	44.815±1.03	1.115±0.06	0.07±0	30.985±9.38	0.035±0.01	31.43±0.31	0.01±0	0.54±0.07	15.25±2.69
S38	18.72±3.38	319.445±73.32	1.885±0.54	10.49±1.77	951.68±516.50	0.975±0.15	21.175±0.90	7.39±3.38	8.375±0.05	42.06±1.40	0.125±0.02	BDL	22.695±0.01	0.86±0.01	0.06±0	28.635±7.06	0.025±0.01	13.96±0.58	0.015±0.01	0.53±0.14	13.625±0.46
S39	20.445±8.55	64.195±6.30	1.245±1.08	9.455±5.49	332.115±5.68	0.72±0.16	19.895±3.06	9.755±10.37	12.675±11.84	37.8±3.55	BDL	BDL	22.055±11.07	0.77±0.13	0.06±0	47.375±31.37	0.14±0.10	10.55±4.36	BDL	0.49±0	14.275±10.83
S40	15.79±2.30	79.725±17.40	0.5±0	10.245±3.53	274.485±5.45	0.8±0.03	18.06±3.20	10.025±8.89	6.755±1.18	37.24±6.12	0.13±0.08	BDL	8.805±0.05	0.7±0.13	0.06±0	28.935±6.06	0.03±0.01	7.46±0.10	BDL	6.86±0	4.485±0.28
S41	13.86±2.64	61.555±0.16	0.545±0.02	7.855±2.75	281.98±22.46	0.81±0.14	18.12±2.97	6.83±7.16	9.345±5.25	37.065±5.13	0.075±0.02	BDL	8.81±0.64	0.72±0.14	0.06±0	31.795±5.04	0.025±0.01	7.18±0.76	BDL	0.4±0	4.055±1.14
Min	5.535	57.255	0.5	4.065	152.86	0.495	9.1	2.53	3.85	18.995	BDL	BDL	5.215	0.495	BDL	13.215	0.025	4.88	BDL	BDL	3.23
Max	26.285	492.15	13.935	223.415	1017.145	1.425	22.475	37.125	14.405	45.395	0.3	0.605	182.665	1.115	0.08	47.375	1.31	60.965	0.04	8.715	29.52
WHO (2011)	2400	1500	15	400	50000	n/a	70	5000	3000	50	10	40	1500	70	3	n/a	20	700	6	10	5 to 25
SANS (2015)	≤ 2400	≤ 300	≤ 200	≤ 400	≤ 2000	≤ 500	≤ 70	≤ 5000	≤ 5000	≤ 50	≤ 10	≤ 40	≤ 1500	≤ 70	≤ 3	n/a	≤ 20	≤ 700	≤ 6	≤ 10	N/A





**Appendix 4: Wet season concentration and SD of trace elements of sampled springs at Thulamela Municipality**

Sample ID	B (µg/L)	Al(µg/L)	V (µg/L)	Mn (µg/L)	Fe (µg/L)	Co (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)	Cr (µg/L)	As (µg/L)	Se (µg/L)	Sr (µg/L)	Mo (µg/L)	Cd (µg/L)	Sn (µg/L)	Sb (µg/L)	Ba (µg/L)	Hg (µg/L)	Pb (µg/L)	Si (mg/L)
S1	14.25±1.18	74.125±5.48	1.34±0.07	17.77±0.65	268.875±58.99	0.79±0.07	20.09±2.8	2.04±0.93	5.055±2.86	40.975±9.00	0.09±0	BDL	33.25±2.63	0.84±0.21	0.07±0	62.21±11.80	25.37±15.97	14.695±0.83	BDL	BDL	22.095±0.22
S2	12.97±1.58	495.755±605.6	5.8±6.79	131.36±81.33	1737.935±2128.47	3.51±3.31	19.485±2.11	4.665±4.54	5.26±3.37	41.895±5.29	0.135±0.09	BDL	27.45±2.58	0.76±0.155	0.075±0.02	56.775±0.84	81.875±56.95	16.765±14.26	BDL	0.73±0	18±0.98
S3	12.925±0.58	120.285±65.08	2.97±2.72	41.385±35.01	1142.165±1233.15	1.185±0.1	18.02±2.1	4.125±3.5	4.275±1.04	37.89±6.27	0.075±0.01	BDL	23.745±1.45	0.69±0.24	0.06±0	56.83±7.54	27.075±25.40	17.57±0.72	BDL	0.42±0	16.76±0.50
S4	12.925±0.95	120.285±28.03	1.38±0.23	20.97±22.21	410.29±281.33	0.88±0.46	18.83±0.48	2.58±0.65	4.715±0.60	38.535±1.73	0.12±0	BDL	23.315±3.2	0.79±0.04	0.12±0	59.485±4.4	82.675±62.44	16.38±0.15	BDL	BDL	16.76±1.0
S5	14.67±0.11	89.525±28.03	0.435±0.06	10.275±0.34	309.36±34.51	0.815±0.13	20.485±5.32	3.3±0.42	4.625±2.07	39.935±11.51	0.07±0	BDL	57.79±8.44	0.79±0.16	BDL	64.195±12.60	28.71±27.97	85.5±10.88	BDL	0.57±0	9.17±0.70
S6	12.935±0.30	104.82±38.89	1.075±0.67	18.21±1.32	327.76±78.18	0.72±0.06	18.69±0.23	1.9±0.27	5.215±1.42	40.595±1.80	0.125±0.01	BDL	19.425±8.76	0.815±0.13	0.06±0	68.455±9.91	82.025±55.47	17.145±4.88	BDL	0.39±0	11.665±3.2
S7	13.27±0.37	130.42±92.45	0.96±0.72	298.37±383.75	479.75±239.52	2.45±2.25	17.535±2.29	2.215±0.53	5.24±1.88	37.33±4.55	0.07±0.014	BDL	21.94±1.61	0.745±0.016	BDL	57.815±6.62	26.055±22.43	17.58±1.59	BDL	BDL	11.785±0.89
S8	14.785±2.61	133.71±8.98	1.015±0.19	10.51±3.30	386.49±7.02	0.89±0.24	27.38±7.1	2.675±0.06	6.58±0.08	53.02±15.08	0.125±0.04	BDL	34.95±2.13	1.065±0.31	0.1±0	64.55±3.77	99.31±43.98	53.73±1.97	BDL	0.56±0	12.715±0.33
S9	13.53±1.80	275.47±307.25	1.82±1.93	14.345±8.96	614.98±645.206	0.79±0.41	19.45±6.68	5.5275±1.30	13.33±2.37	40.35±15.44	0.135±0.08	BDL	43.695±4.48	0.79±0.26	0.06±0	58.225±4.05	92.955±89.69	77.43±9.93	BDL	0.58±0	11.44±0.65
S10	17.12±5.51	167.03±32.29	1.245±0.45	13.65±9.57	309.5±95.10	1.195±0.94	19.51±8.24	6.94±6.33	9.355±4.62	39.425±15.50	0.1±0.06	BDL	21.445±12.09	0.775±0.33	0.07±0	64.805±8.59	22.985±8.59	24.845±15.13	BDL	0.5±	11.895±9.35
S11	14.32±0.51	194.445±30.455	4.52±0.24	8.37±0.01	521.705±33.14	0.795±0.04	21.035±2.92	2.85±1.00	3.7±0.52	43±2.91	0.12±0.042	BDL	44.55±7.79	0.89±0.04	0.07±0.014	66.805±13.35	91.61±61.16	6.87±2.18	BDL	0.445±0.01	21.815±1.42
S12	22.19±6.41	125.41±58.63	2.635±1.14	9.16±2.62	426.93±155.45	0.845±0.02	26.64±6.18	2.615±0.62	7.315±3.39	50.915±11.82	0.105±0.02	BDL	63.305±16.73	1.075±0.23	0.075±0.02	67.13±6.14	104.2±54.02	17.475±7.67	BDL	0.47±0	24.995±5.53
S13	13.225±0.76	122.46±84.96	1.68±0.44	9.725±0.52	327.81±151.26	0.7±0.04	21.87±4.02	1.705±0.60	5.045±2.21	36.6±8.47	0.08±0	BDL	96.86±3.74	0.75±0.23	0.06±0	58.08±6.49	21.545±12.75	60.805±4.04	BDL	BDL	17.98±0.098
S14	14.865±0.10	93.51±51.18	1.465±0.83	7.015±0.05	265.025±85.21	0.655±0.12	19.975±4.36	1.99±0.22	6.41±1.99	40.625±9.51	0.09±0	BDL	28.65±6.92	0.785±0.15	0.06±0	55.065±5.06	29.53±27.94	12.025±4.98	BDL	BDL	17.305±4.63
S15	14.94±0.99	291.195±156.29	3.245±1.45	47.9±60.0	840.435±663.37	1.15±0.96	17.06±5.78	3.135±1.36	5.475±3.10	34.995±13.59	0.105±0.05	BDL	36.495±5.76	0.705±0.26	BDL	59.015±1.11	63.21±24.57	14.245±3.30	BDL	0.84±0	21.84±1.78
S16	14.365±1.94	356.89±426.66	4.805±0.60	6.395±0.47	352.66±226.19	0.61±0.04	16.47±0.14	1.79±0.18	3.84±0.51	34.675±0.75	0.135±0.01	BDL	135.19±2.77	0.905±0.12	0.07±0	60.465±1.61	68.39±50.72	28.85±0.59	BDL	BDL	28.8±1.4
S17	15.545±1.14	243.13±267.94	5.2±1.39	19.395±22.04	757.59±796.12	1.105±0.89	18.49±2.74	1.895±0.34	4.46±0.63	39.645±6.23	0.115±0.02	BDL	133.635±1.18	1.085±0.02	0.04±0.02	73.495±14.62	26.11±18.87	33.535±2.29	BDL	0.55±0	28.75±0.24
S18	12.19±1.53	554.13±585.38	5.97±2.26	11.74±7.22	868.35±797.46	0.975±0.04	21.03±0.83	2.79±0.03	4.895±1.82	49.07±3.13	0.125±0.01	BDL	117.51±2.44	0.925±0.05	0.06±0	54.235±4.07	28.125±21.77	77.61±12.24	BDL	1.245±0.76	17.825±1.08
S19	12.12±0.34	67.1±8.37	1.79±0.31	4.625±0.88	192.02±6.71	0.53±0	16.815±1.45	1.27±0.18	6.175±2.17	35.085±4.36	0.1±0	BDL	93.095±14.36	0.735±0.06	BDL	57.475±10.03	23.785±21.17	70.4±12.71	BDL	BDL	17.175±0.60
S20	19.995±0.93	209.165±233.61	3.78±1.32	42.055±51.22	605.72±672.40	0.865±0.70	14.78±3.25	2.31±1.57	3.78±0.65	29.815±7.89	0.08±0	BDL	73.275±2.97	0.6±0.14	BDL	58.91±10.67	18.055±10.84	29.825±25.36	BDL	BDL	24.025±3.69
S21	47.255±3.23	84.715±26.92	14.9±0.76	72.955±11.34	268.91±138.53	1.465±0.18	22.475±6.27	3.925±0.01	10.015±4.8	43.87±15.16	0.145±0.04	0.605±0.09	197.565±6.28	1.735±0.11	0.08±0.014	53.995±4.19	82.485±35.97	29.735±0.19	BDL	0.42±0	36.195±0.61

S22	21.11±1.88	149.87±47.57	4.03±0.11	23.875±8.90	490.915±12.18	0.805±0.19	18.08±3.39	3.445±0.10	5.08±2.05	38.445±5.72	0.145±0.06	0.19±0	79.49±7.99	0.825±0.05	0.08±0	73.86±5.52	88.375±73.12	37.57±5.46	BDL	BDL	19.905±0.28
S23	15.5±0.11	144.97±103.74	5.125±0.66	22.345±11.12	450.08±315.16	1.01±0.44	20.145±1.21	3.085±0.19	10.425±4.5	40.31±3.32	0.105±0.01	BDL	85.005±3.68	0.875±0.01	0.065±0.01	61.965±3.6	83.79±54.37	8.155±1.63	BDL	0.53±0	31.595±0.75
S24	24.59±3.79	163.04±47.34	7.055±0.54	35.8±34.41	544.215±236.35	1.05±0.54	19.53±3.38	2.9±0.78	6.065±2.5	36.565±5.96	0.12±0.04	BDL	55.98±3.01	0.695±0.11	0.06±0	56.63±2.78	68.355±39.8	8.725±4.09	BDL	BDL	26.17±0.28
S25	22.26±1.70	80.325±5.45	1.925±0.01	7.51±2.01	243.595±62.27	0.59±0.023	18.295±0.05	25.625±32.87	22.11±19.71	38.77±0.80	0.105±0.02	BDL	25.07±0.94	0.755±0.04	0.07±0	54.34±1.28	78.295±54.68	12.165±0.96	0.01±0	0.885±0.64	28.345±0.84
S26	25.295±2.11	65.625±23.92	2.075±0.45	12.85±1.46	246.75±48.06	0.73±0.06	19.725±0.57	1.625±0.049	3.925±0.84	42.225±0.33	0.07±0	BDL	35.925±1.04	0.825±0.06	0.09±0	59.33±2.48	28.485±21.38	15.975±0.64	BDL	0.4±0	28.345±0.37
S27	25.15±2.87	103.63±32.13	2.46±0.08	16.365±11.03	323.625±98.58	0.73±0.17	20.07±4.86	2.56±0.69	6.615±3.06	42.585±9.75	0.105±0.035	BDL	31.865±0.77	0.835±0.148	0.08±0	56.745±9.08	95.485±82.54	17.46±1.06	BDL	0.41±0	27.665±0.68
S28	12.785±0.23	133.795±12.52	1.185±0.05	10.51±4.6	365.2±37.09	0.725±0.12	18.3±1.83	1.86±0.42	4.39±0.28	38.855±3.86	0.1±0.03	BDL	19.63±0.59	0.725±0.135	0.065±0.01	63.85±10.63	79.61±61.27	15.755±2.52	BDL	BDL	11.955±0.44
S29	13.09±4.30	172.01±72.11	1.945±1.62	12.68±5.41	388.115±201.51	1.02±0.07	23.075±1.11	2.94±1.07	8.635±0.92	48.89±1.866	0.08±0.014	BDL	27.04±27.25	0.965±0.05	0.07±0	58.72±4.43	31.045±23.44	11.195±3.311	BDL	0.5±0.08	15.815±15.39
S30	13.375±1.94	109.07±58.73	1.085±0.10	14.755±13.58	238.09±58.28	0.79±0.45	14.425±1.49	7.675±5.96	7.28±1.13	31.245±4.89	0.0667±0	BDL	15.845±9.60	0.6±0.042	0.07±0	55.36±6.56	63.135±49.98	14.11±3.6	BDL	0.42±0	9.315±5.45
S31	12.535±1.72	172.530±306.41	3.12±1.82	19.91±7.57	609.06±225.71	0.93±0.014	19.585±0.61	3.315±1.12	6.3±2.0	42.285±2.1	0.15±0.014	BDL	9.1±0.45	0.725±0.05	0.075±0.01	55.625±4.29	80.36±59.99	11.925±1.67	BDL	0.475±0.08	5.43±0.014
S32	20.185±15.54	165.08±136.23	1.83±2.12	33.435±8.66	692.75±632.38	1.175±0.21	20.8±3.36	2.64±0.64	6.46±1.81	43.32±6.39	0.2±0.07	BDL	12.505±9.7	0.865±0.233	0.07±0.014	61.695±14.77	93.03±79.56	14.78±4.79	BDL	0.39±0	5.435±2.41
S33	12.06±2.12	111.875±51.41	0.595±0.13	6.41±2.22	261.185±76.75	0.725±0.26	23.765±7.12	2.115±0.98	6.94±5.23	50.785±15.72	0.11±0	BDL	12.045±2.64	0.975±0.25	0.07±0.014	68.48±16.01	38.265±36.30	12.3±2.98	BDL	0.47±0	5.355±0.06
S34	22.45±3.93	116.39±47.32	1.805±1.11	11.035±6.92	360.4±166.65	1.355±0.233	25.63±10.34	2.315±0.3	61.675±19.98	51.26±23.99	0.1±0.014	BDL	34.015±12.76	1.08±0.49	0.065±0.01	57.065±20.72	92.605±26.33	13.155±1.9	BDL	0.57±0	16.8±3.52
S35	21.245±2.50	231.145±173.72	2.635±0.83	21.335±7.191	567.61±566.69	0.855±0.26	16.305±0.62	2.82±1.48	7.43±2.91	32.25±3.54	0.135±0.06	BDL	16.88±5.2	0.545±0.07	BDL	57.065±9.91	56.75±34.76	10.855±0.06	BDL	0.43±0	6.615±0.02
S36	17.075±7.32	114.45±14.91	1.36±0.86	20.35±2.87	274.095±43.84	0.825±0.90	21.54±2.57	2.615±1.67	7.2±5.25	43.27±5.28	0.08±0.02	BDL	16.015±5.16	0.88±0.11	0.085±0	58.19±12.3	27.17±18.79	11.635±0.37	BDL	BDL	7.15±1.1
S37	30.905±0.88	86.12±19.10	7.51±1.50	22.105±17.81	435.825±102.52	1.34±0.31	16.5±0.69	2.395±1.11	5.43±2.29	35.515±2.64	0.33±0.014	BDL	48.925±2.06	0.97±0.03	BDL	56.605±4.36	72.895±48.68	34.58±0.45	BDL	BDL	18.715±0.56
S38	25.32±0.40	956.01±485.56	10.93±3.55	58.86±37.9	4532.72±6788.87	3.02±1.3	23.46±3.07	5.745±0.42	6.865±1.99	41.37±8.6	0.515±0.11	BDL	28.445±1.73	0.61±0.141	BDL	55.32±13.76	18.75±10.22	21.97±4.8	0.04±0.04	0.995±0.18	18.805±0.34
S39	22.365±2.31	116.84±70.92	0.8±0.40	10.315±4.77	445.94±223.08	0.82±0.11	23.34±8.72	2.025±0.53	4.19±1.54	43.455±11.25	0.11±0.04	BDL	14.155±1.87	0.975±0.36	0.06±0	58±2.74	83.015±38.38	8.885±1.44	0.01±0	0.01±0	7.8±0.11
S40	18.135±1.08	121.54±51.15	0.69±0.01	15.5±9.23	347.685±83.27	1.455±0.62	21.215±0.62	3.345±1.32	6.595±2.46	46.285±4.51	0.17±0.07	BDL	11.52±3.04	0.88±0.09	0.065±0.01	61.84±14.69	90.35±57.97	23.25±20.30	BDL	0.4±0	5.785±0.75
S41	16.46±2.88	78.22±9.18	1.06±0.065	13.365±3.85	404.535±161.72	0.82±0.04	24.035±2.11	8.41±9m66	8.76±7.39	47.915±0.54	0.115±0.05	BDL	24.265±	1.09±0.141	0.07±0.014	65.94±3.59	36.185±25.47	13.945±5.79	BDL	0.625±0.30	11.83±9.8
Min	21.11	78.22	0.435	4.625	192.02	0.59	14.78	1.27	3.7	29.815	0.07	BDL	9.1	0.6	BDL	53.995	18.055	6.87	BDL	BDL	5.43
Max	47.255	2612.745	10.93	298.37	4532.72	1.465	24.035	25.625	61.675	53.02	0.515	0.605	197.565	1.735	0.12	68.48	104.2	60.805	0.04	0.995	36.195
WHO (2011)	2400	1500	15	400	50000	n/a	70	5000	3000	50	10	40	1500	70	3	n/a	20	700	6	10	
SANS (2015)	≤ 2400	≤ 300	≤ 200	≤ 400	≤ 2000	≤ 500	≤ 70	≤ 5000	≤ 5000	≤ 50	≤ 10	≤ 40	≤ 1500	≤ 70	≤ 3	n/a	≤ 20	≤ 700	≤ 6	≤ 10	



**Appendix 5: Statistical Analysis of Dry Season Correlation coefficient results**

	Temp	pH	Salinity	TDS	Turbidity	EC	TC	FC	E.Coli	Fe	Mn	Co	Ni	Cu	Zn	Cr	Mo	Ba	Na	Mg	Si	Ca	Cl	NO3	B	Al	V	Sr	Sn	Sb
Temp	1.00																													
pH	-0.24	1.00																												
Salinity	-0.05	-0.08	1.00																											
TDS	-0.02	-0.15	<b>0.83</b>	1.00																										
Turbidity	0.25	-0.11	-0.30	-0.28	1.00																									
EC	0.07	-0.20	<b>0.76</b>	<b>0.95</b>	-0.28	1.00																								
Total C	-0.14	-0.13	0.35	0.26	0.35	0.24	1.00																							
Faecal C	0.26	-0.04	-0.22	-0.16	0.24	-0.16	0.01	1.00																						
E.Coli	0.14	0.15	0.09	0.06	-0.09	0.06	-0.07	<b>0.52</b>	1.00																					
Fe	0.06	0.10	-0.27	-0.21	<b>0.70</b>	-0.25	0.13	0.20	0.06	1.00																				
Mn	-0.22	-0.04	0.47	<b>0.54</b>	-0.13	0.43	0.08	-0.17	-0.05	0.09	1.00																			
Co	-0.04	0.19	0.40	0.40	-0.02	0.29	-0.03	0.01	0.04	0.38	0.48	1.00																		
Ni	0.37	-0.17	0.08	0.07	-0.08	0.09	-0.28	0.04	0.03	0.06	-0.22	0.16	1.00																	
Cu	-0.10	0.15	-0.10	-0.02	0.07	-0.20	-0.14	0.08	0.05	0.23	-0.01	0.16	0.30	1.00																
Zn	0.01	-0.24	0.03	0.12	-0.11	0.09	-0.30	0.02	-0.06	-0.06	0.23	0.22	0.29	0.24	1.00															
Cr	0.49	-0.13	-0.12	-0.05	0.00	-0.01	-0.37	0.16	0.10	0.16	-0.28	0.07	<b>0.91</b>	0.30	0.10	1.00														
Mo	0.27	-0.11	0.43	<b>0.51</b>	-0.09	0.46	-0.11	-0.06	0.10	-0.11	0.09	0.37	0.49	0.34	0.32	0.41	1.00													
Ba	-0.08	0.17	-0.10	0.01	-0.22	-0.04	-0.22	0.01	-0.02	-0.09	-0.04	-0.02	0.30	0.35	0.08	0.27	0.27	1.00												
Na	-0.02	-0.13	<b>0.81</b>	<b>0.91</b>	-0.22	<b>0.84</b>	0.31	-0.23	-0.02	-0.15	0.48	0.38	0.14	0.11	0.13	0.00	<b>0.64</b>	0.10	1.00											
Mg	-0.06	-0.18	<b>0.81</b>	<b>0.96</b>	-0.25	<b>0.88</b>	0.26	-0.13	0.03	-0.18	<b>0.57</b>	0.48	0.06	0.05	0.27	-0.09	<b>0.55</b>	-0.03	<b>0.91</b>	1.00										
Si	0.08	-0.04	<b>0.60</b>	<b>0.78</b>	-0.25	<b>0.74</b>	0.26	0.05	0.24	-0.18	0.28	0.21	0.08	0.11	0.09	0.06	<b>0.52</b>	0.03	<b>0.73</b>	<b>0.75</b>	1.00									
Ca	-0.06	-0.16	<b>0.79</b>	<b>0.97</b>	-0.29	<b>0.91</b>	0.26	-0.11	0.09	-0.16	<b>0.60</b>	0.43	0.00	0.00	0.20	-0.10	<b>0.50</b>	-0.05	<b>0.90</b>	<b>0.97</b>	<b>0.79</b>	1.00								
Cl	-0.04	-0.30	<b>0.76</b>	<b>0.87</b>	-0.20	<b>0.80</b>	0.28	-0.18	-0.10	-0.18	<b>0.57</b>	0.41	0.05	-0.08	0.18	-0.08	0.36	-0.08	<b>0.82</b>	<b>0.91</b>	<b>0.56</b>	<b>0.88</b>	1.00							
NO3	0.13	-0.18	<b>0.66</b>	<b>0.70</b>	-0.23	<b>0.65</b>	0.24	-0.01	0.04	-0.27	0.18	0.29	0.09	-0.11	0.12	-0.04	0.21	-0.11	<b>0.56</b>	<b>0.70</b>	<b>0.50</b>	<b>0.66</b>	<b>0.76</b>	1.00						
B	0.38	-0.16	0.44	0.46	0.00	0.44	0.00	0.01	-0.02	-0.06	0.21	<b>0.52</b>	0.22	0.01	0.40	0.09	<b>0.63</b>	-0.16	<b>0.54</b>	<b>0.58</b>	0.33	<b>0.50</b>	0.48	0.39	1.00					
Al	0.17	-0.12	-0.32	-0.34	<b>0.72</b>	-0.39	0.27	0.25	-0.08	<b>0.76</b>	-0.10	0.22	0.01	0.17	-0.17	0.07	-0.30	-0.22	-0.33	-0.31	-0.36	-0.34	-0.22	-0.17	-0.08	1.00				
V	0.20	-0.04	<b>0.55</b>	<b>0.68</b>	0.02	<b>0.62</b>	0.21	0.03	0.09	0.08	0.23	<b>0.54</b>	0.16	0.26	0.06	0.11	<b>0.70</b>	0.02	<b>0.69</b>	<b>0.67</b>	<b>0.57</b>	<b>0.66</b>	0.49	0.38	<b>0.66</b>	0.06	1.00			
Sr	-0.08	0.05	<b>0.60</b>	<b>0.72</b>	-0.22	<b>0.58</b>	0.21	-0.07	0.07	-0.15	0.32	0.34	0.15	0.41	0.05	0.07	<b>0.67</b>	0.41	<b>0.79</b>	<b>0.73</b>	<b>0.72</b>	<b>0.69</b>	<b>0.60</b>	0.38	0.33	-0.30	<b>0.66</b>	1.00		
Sn	0.07	-0.11	-0.25	-0.20	0.07	-0.16	-0.22	0.02	0.04	0.17	-0.10	-0.16	0.05	0.06	0.18	0.06	-0.13	-0.04	-0.15	-0.12	-0.28	-0.15	-0.14	-0.15	0.00	0.04	-0.25	-0.27	1.00	

Sb	-0.15	0.16	0.26	0.29	-0.01	0.26	0.32	0.03	-0.12	-0.13	0.16	0.09	-	-0.12	-0.07	-0.20	0.09	-0.04	0.27	0.25	0.41	0.26	0.15	0.05	0.08	-0.10	0.31	0.34	-0.64	1.00
													0.16																	

**Appendix 6: Statistical Analysis of Wet Season Correlation coefficient results**

	Temp	pH	Salinity	TDS	Turbidity	EC	TC	FC	E.Coli	Fe	Mn	Co	Ni	Cu	Zn	Cr	Mo	Ba	Na	Mg	Si	Ca	Cl	NO3	B	Al	V	Sr	Sn	Sb
Temp	1.00																													
pH	-0.04	1.00																												
Salinity	0.07	-0.03	1.00																											
TDS	0.03	-0.05	<b>0.67</b>	1.00																										
Turbidity	0.11	0.34	-0.16	-0.15	1.00																									
EC	0.07	-0.12	<b>0.90</b>	<b>0.87</b>	-0.23	1.00																								
TC	0.06	0.32	0.27	0.29	0.18	0.28	1.00																							
FC	0.02	-0.11	0.04	0.19	-0.07	0.09	-0.16	1.00																						
E.Coli	0.01	-0.22	0.12	0.22	-0.09	0.20	0.03	<b>0.61</b>	1.00																					
Fe	-0.19	0.28	-0.08	-0.08	0.07	-0.10	0.22	-0.18	-0.18	1.00																				
Mn	0.20	0.11	0.09	0.10	0.07	-0.02	0.15	0.32	0.26	0.13	1.00																			
Co	-0.13	0.05	-0.02	-0.01	-0.01	-0.04	-0.06	0.06	0.04	<b>0.64</b>	0.45	1.00																		
Ni	0.01	-0.22	0.31	0.38	-0.17	0.36	-0.08	0.24	0.18	0.03	0.10	-0.04	1.00																	
Cu	-0.02	-0.11	-0.27	-0.23	0.21	-0.32	-0.08	-0.04	-0.08	0.08	-0.09	-0.05	0.10	1.00																
Zn	0.01	-0.12	0.24	0.31	0.08	0.33	0.04	-0.01	0.13	-0.13	-0.08	0.04	0.19	0.07	1.00															
Cr	-0.18	-0.34	-0.11	-0.13	-0.09	-0.09	-0.30	-0.23	-0.12	0.04	-0.36	0.09	0.34	0.34	0.27	1.00														
Mo	-0.06	-0.06	0.14	0.18	0.30	0.15	0.02	-0.19	-0.22	-0.15	0.03	0.08	0.19	0.31	0.23	0.41	1.00													
Ba	-0.14	0.04	-0.13	-0.12	-0.19	-0.15	-0.17	-0.01	-0.08	-0.06	-0.08	-0.12	0.10	0.25	-0.07	0.16	0.16	1.00												
Na	0.23	0.11	0.35	0.46	0.19	0.38	0.39	0.00	0.01	-0.13	0.30	-0.01	0.17	-0.05	0.07	-0.11	<b>0.63</b>	0.17	1.00											
Mg	0.33	0.17	0.31	0.41	0.29	0.32	0.40	-0.01	0.01	-0.12	0.38	0.01	0.18	-0.03	0.11	-0.15	<b>0.60</b>	-0.01	<b>0.92</b>	1.00										
Si	0.15	0.07	0.18	0.40	0.35	0.27	0.19	-0.07	-0.01	-0.02	0.15	-0.01	0.12	0.09	0.05	-0.03	0.46	-0.04	<b>0.65</b>	<b>0.71</b>	1.00									
Ca	0.38	0.14	0.29	0.44	0.25	0.32	0.36	0.00	0.04	-0.16	0.39	-0.02	0.18	-0.07	0.04	-0.16	<b>0.54</b>	-0.05	<b>0.89</b>	<b>0.96</b>	<b>0.77</b>	1.00								
Cl	0.46	0.12	0.29	0.41	0.15	0.32	0.37	0.01	0.01	-0.08	0.31	0.00	0.22	-0.06	0.08	-0.08	<b>0.50</b>	-0.04	<b>0.87</b>	<b>0.93</b>	<b>0.60</b>	<b>0.89</b>	1.00							
NO3	0.38	0.00	0.41	<b>0.51</b>	-0.05	0.49	0.33	0.11	0.25	-0.23	0.11	-0.17	0.30	-0.18	0.13	-0.11	0.27	0.08	<b>0.74</b>	<b>0.75</b>	<b>0.56</b>	<b>0.73</b>	<b>0.82</b>	1.00						
B	-0.06	0.23	0.31	0.28	<b>0.51</b>	0.29	0.30	-0.08	-0.08	0.05	0.21	0.14	0.20	0.02	0.28	0.06	<b>0.63</b>	-0.14	<b>0.58</b>	<b>0.67</b>	0.45	<b>0.59</b>	<b>0.52</b>	0.32	1.00					

Al	-0.28	0.26	-0.02	0.02	0.01	0.00	0.19	-0.12	-0.16	<b>0.94</b>	0.06	<b>0.59</b>	0.11	0.07	-0.06	0.11	-0.07	0.02	-0.05	-0.06	0.05	-0.13	-0.01	-0.13	0.10	1.00						
V	0.00	0.37	0.17	0.26	0.40	0.18	0.40	-0.17	-0.16	0.45	0.28	0.44	0.07	0.12	-0.04	0.00	<b>0.58</b>	0.02	<b>0.65</b>	<b>0.67</b>	<b>0.58</b>	<b>0.64</b>	<b>0.57</b>	0.32	<b>0.66</b>	0.48	1.00					
Sr	0.08	0.09	0.22	0.35	0.12	0.24	0.28	-0.07	-0.08	-0.11	0.18	-0.08	0.12	0.24	-0.06	-0.03	<b>0.65</b>	0.44	<b>0.79</b>	<b>0.74</b>	<b>0.66</b>	<b>0.70</b>	<b>0.65</b>	<b>0.59</b>	0.36	0.00	<b>0.62</b>	1.00				
Sn	0.19	-0.27	0.09	0.08	-0.35	0.03	-0.07	-0.01	-0.14	-0.14	0.01	-0.23	0.08	0.07	-0.15	0.20	0.09	0.02	0.09	0.01	-0.06	0.05	0.15	0.03	-0.24	-0.18	-0.26	0.04	1.00			
Sb	0.11	-0.08	0.13	-0.06	0.11	0.02	0.04	-0.22	-0.08	-0.15	-0.06	-0.05	-0.12	0.00	0.28	0.15	0.18	-0.19	0.16	0.18	0.04	0.16	0.17	0.07	0.23	-0.21	0.05	-0.08	0.10	1.00		

**Appendix 7: Spring water sampled from**





Duthuni B Tshigulw



Duthuni B Tshotolokwe



Duthuni M Tshiseluselu



Duthuni Lwandani



Dzindi



Lwamondo mutandani



Makwarela



Mavhunda



Mavhunda 2



Shanzha



Mandala



Tshakhuma Tshiomva A



Tshakhuma Tshiomva B



Tshifulanani Madzhatshise



Mungani Sasol



Makhuvha Zwidengani



Ngovhela Down