University of Venda

Faculty of Science, Engineering and Agriculture

ASSESSMENT OF HEALTH RISK ASSOCIATED WITH GROUNDWATER FROM COLLINS CHABANE AND MAKHADO MUNICIPALITY OF VHEMBE DISTRICT

A Dissertation submitted to the Department of Earth Sciences in fulfilment for the award of Masters of Earth Sciences degree in Hydrology and Water Resources

By

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Dedication

It is with sincere gratitude and warm regard that I dedicate this work to my son Rei Mutileni and father the late Mr J. Malan Mutileni

Declaration

I, **Mutileni N** declare that this dissertation submitted to the Department of Earth Sciences of the University of Venda in fulfillment of the requirements for the master's degree of Earth Sciences in Hydrology and Water Resources has not been submitted to any university. This is my work in design and implementation and all references cited have been fully acknowledged in the text and in the list of references.

Signature……   Date………12/10/2021…………

N. MUTILENI

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Abstract

Water is essential to life, but many people lack access to clean and safe drinking water, and many die of preventable waterborne diseases. The study conducted assessed groundwater vulnerability to Physico-chemical and microbial contamination across the Collins Chabane and Makhado Municipality. A three-set of samples (for metals, non-metals and microbial analysis) were randomly collected from twenty (20) primary schools, fifteen (15) private boreholes, and three (3) communal boreholes of Vhembe district, Limpopo province, South Africa. The physicochemical water quality parameters (pH, EC, and TDS) were measured using the YSI Professional Plus meter . At the same time, turbidity and salinity were measured using an Orbeco-Hellige portable turbidimeter and Extech multimeter, respectively. The physicochemical parameters measure in the field comply with the recommended standard set by South African Nation Standard SANS (2015) apart from the pH value detected in one sample collected in the wet season. Nitrate concentration (2.03–1532 mg/L) was obtained in high values in the most sample in the wet season. Some boreholes can have a noticeable taste due to chloride concentration (14.12–690 mg/L).

The following metals Cd, Pb, Hg, As, Al, Mn, Fe, Co, Ni, Cu, Cr and Zn, Ca, K, Mg, and Na were analysed using an Inductively coupled plasma Mass spectrometer. The analytical results for major cations i.e., Ca, Mg, K and Na range between 14.20 – 349 mg/L, 11.40 – 309 mg/L, 0.49–12.80 mg/L, and 13.60 – 97.80 mg/L, respectively. The high concentration of Ca and Mg recorded in some of the sites exceeded the recommended limit set by DWAF (1996) and WHO (2015). The analytical results of heavy metal indicated that Ni (16.35 – 308.53 µg/L), Cr (27.46 – 72.84 µg/L), and Al (0.14 – 0.76 mg/L) were above the standard limits of SANS 241 (2015) in some of the sites.

The membrane filtration method was employed to determine faecal indicator organisms. The results obtained for E. *coli* ranged between 0.0 – 76 cfu/100 ml in the dry season, while numerous values were detected for total coliform in both dry and wet season. All borehole failed to comply with SANS 241 and WHO standard limit in terms of total coliform while, 42.11% of borehole failed to comply with SANS 241 in terms of *E. coli*.

Groundwater geochemistry was evaluated through Gibb's diagram and Piper plot. The most dominant water type across all groundwater sample was $Mg\text{-}HCO_3$ (40.79%, n=76) and Mg-Cl water type (38.16%, n=76) throughout the study period. Twenty one parameters (pH, EC, Cl^-, NO_3^-, F^-, SO_4^{-2}, HCO_3^-, Ca, Mg, K Na, Total Hardness as $CaCO_3$, Cr, Mn, Co, Ni, Cu, Zn, Hg, Pb and Fe) were taken into consideration for the computation of water quality index (WQI). The WQI values of the selected school, household, and communal samples (50-103 and 25-101, 26-485 and 21-442, and 35-57 and 50-56, respectively) fell between the excellent to poor, excellent to unsuitable and excellent to good water based on the physico-chemical parameters used during dry and wet season, respectively. Some household samples had poor (21.43%), and unsuitable water (10.71%) during the assessment period. Nitrate was the principal element with enormously high concentrations that violated the WHO and SANS 241 permissible limit for drinking purpose which caused high levels of WQI. The source of contamination could be anthropogenic activities.

Human health risk associated with the water quality parameters assessed was calculated using non-carcinogenic effects using hazard quotient toxicity potential (HQ_{ing}), cumulative hazard index (HI) and daily human exposure dose (D_{ing}) of drinking water through ingestion pathway. The computed non-carcinogenic effects (HQ_{ing}) and HI for children and adult were ≥ 1 throughout the assessment. The main contributors to non-carcinogenic health risks in this investigation were Cr, Hg, and As. The carcinogenic risk assessment evaluated from selected heavy metals (Cr, Cd, Hg, Pb and As) exceeded the suggested potential risk limits apart from As and Hg for Adult in Dry season. Cr and Pb were above the carcinogenic indices of 1E-04 and 1E-06 throughout the season. Hence, these parameters can pose potential risk to both age group. Therefore, preventive measure should be implemented to prevent long term cumulative exposure risk. Quantitative microbial risk assessment (QMRA) was carried out to determine the risks of infection and illness due to consumption of groundwater. The estimation of QMRA indices values suggest that school boreholes had higher risk of infection than household and communal sites. Highest risk of infection has been detected during the month of November (wet season) in 2019. Only 30% school boreholes had an extremely high annual risk (90.52-100% probability) of *E. coli* infections to children. High probability values (90.5-100% probability) for annual risk of infection in all age group has been observed in 35.90% school samples throughout the assessment. Only 10.26% of school samples had annual risk of illness probability value of 35% in all age group. The annual risk of *E. coli* infections and illness was high in household site with 100% and 35% for all age group respectively. Meanwhile, 80.94 and 28.33% were the highest maximum values assessed for infection and illness in communal site. The estimation of QMRA indices suggest groundwater from the investigated study being a hazard.

The methods of analysis in this study, suggested possible contamination of groundwater by anthropogenic activities such as small-scale agricultural activities, faecal contamination (pit latrines and septic storage), domestic waste on land, waste from concentrated livestock and natural processes such as microbial interference, weathering and dissolution. Preventive and mitigation measures to minimise such risks are indispensable.

Keywords: Water Quality Index, Health Risk Assessment, Hydrogeochemistry, Correlation, Quantitative Microbial Risk Assessment

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Glossary of Abbreviations

AAS	Atomic Absorption spectrometry
AES	Atomic Emission Spectroscopy
Al	Aluminium
Ca	Calcium
CDI	Chronic Daily Intake
Cl^-	Chloride
Co	Cobalt
Cr	Chromium
Cu	Copper
DWAF	Department of Water Affairs and Forestry
E.*Coli*	Escherichia Coli
EC	Electric Conductivity
EPA	Environmental Protection Agency
F^-	Fluoride
GSS	Geochemistry’s Spread Sheet
HCO_3^-	Bicarbonate
Hg	Mercury
HI	Hazard Index
HQ	Hazard Quotient
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
Mg	Magnesium
Mn	Manganese
Na	Sodium

Ni	Nickel
NO_3^-	Nitrate
Pb	Lead
SANS	South African National Standard
SO_4^{2-}	Sulphate
USEPA	United State of Environmental Protection Agency
WHO	World Health Organization
WRC	Water Research Commission
Zn	Zinc

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CHAPTER 1: INTRODUCTION

1.1 Background

Clean and safe drinking water is essential for human health. Unfortunately, many people still live without sustainable access to potable water. Such people often resort to other sources of water to meet their water demand (Edokpayi et al., 2018a). Surface and groundwater are often used as alternative water sources. According to Fetter (2001), more than 98% of available fresh water accessible to humans is groundwater, exceeding the amount of surface water. There is high vulnerability threat to surface water than groundwater due to various sources of pollution (Sasakova et al., 2018). Therefore, groundwater is usually preferred to surface water for domestic purposes because of its perceived better quality. Due to this facts, available groundwater resource (around 7500 million m^3/a) is extensively being utilized in rural and urban areas of South Africa (Department Water and Sanitation (DWS), 2016).

Groundwater occurrence is often in the form of transboundary aquifer systems. The aquifers spread over tens to hundreds of kilometers meaning they are not limited to any human-made boundaries (Struckmeier et al., 2006). The type of soil as well as the thickness of the sediments helps distinguish the aquifers' ability to store water (Salako and Adepelumi, 2018). This means that different aquifers have different storage capacities as well as water qualities. This is because the soil acts as a filter which reduces the number of microbial contaminants in the water (Appelo and Postma, 2005). However, report have shown that contamination of groundwater could be through both chemical and biological agents (Sasakova et al., 2018). Contamination sources includes discharge of domestic wastes on land and streams, natural runoff after rainfall events, effluents from wastewater treatment facilities, agricultural and industrial effluents and several other anthropogenic activities (Pawari and Gawande, 2015; Alrumman *et al.,* 2016; Haseena *et al.,* 2017).

Water extracted from government schools and clinics, hospitals as well as private boreholes (resident owners, shopping centres, both agricultural and poultry farms, schools, hotels and lodge) are consumed or used without treatment. Insufficient allocation of government funds and inadequate human resources results in limited or no access to suitable sanitation and water treatment services which lead the community to rely on untreated ground water without considering the possible potential sources of groundwater contamination of physico-chemical and microbial parameters (Obi *et al.,* 2002; Makungo and Odiyo, 2018).

Most important threats to public health by the consumption of such contaminated groundwater is the presence of elevated concentration of heavy metals, major anion and pathogens putting the health of the people who consume and use the groundwater for agricultural and recreational purposes under threat (Pawari and Gawande, 2015, Itoba-Tombo et al., 2017).

Waterborne diseases infection has increase drastically since early 2000 in South Africa (DWA, 2002; Bessong *et al.,* 2009). There is a possibility of 43, 000 death annually in South Africa (SA) due to diarrhoea diseases (Edokpayi *et al*., 2018a). Most rural societies in South Africa rely on untreated or insufficiently treated water from ground and surface resources such as dams, rivers, lakes and aquifers for their daily supply and have limited or no access to satisfactory sanitation facilities (Edokpayi *et al*., 2018a). Hence, the community are at high risk of waterborne diseases (DWA, 2002). Waterborne diseases could be transmitted through both ingestion and dermal exposure to contaminated groundwater, such as swimming in pools filled with contaminated groundwater, through bathing, drinking and eating uncooked vegetables/fruits irrigated with contaminated groundwater (Pawari and Gawande, 2015; Haseena *et al*., 2017).

Numerous villages of Limpopo province rely on borehole water supplies which were confirmed to be contaminated by microorganisms (Holland, 2011; Edokpayi et al., 2018b). In the Tshitale village of Hlanganani region and Muledane Block J of Vhembe District Municipality of Limpopo Province, boreholes are drilled within the vicinity of pit latrines, burial site, wastes disposal and subsistence farms which are known causes of high microbial contamination to groundwater (Potgieter et al., 2006; Makungo and Odiyo, 2018; Edokpayi et al., 2018b). Similar cases have been reported in rural areas across Africa and outside the continent such as Zimbabwe, South West Nigeria, Bihar State in India, amongst others (Dzwairo et al., 2006; Adekunle et al., 2007; Sorensen et al., 2016).

1.2 Problem statement

Majority of people in rural areas depend on groundwater for domestic purposes due to its quality, widespread distribution, and low development cost (Howard *et al.,* 2006). However, anthropogenic activities have significantly affected the quality and accessibility of groundwater (Kac¸arog˘lu and Gu¨nay, 2012). Rural communities are likely to be exposed more frequently to higher levels of heavy metals and anions pollution due to supply and consumptions of untreated groundwater due. Due to erratic supply of treated municipal water, the investigated community including their primary schools rely on untreated groundwater.

The investigated study area consist of rural dwellers and primary school learners who uses both pit latrine and flush toilets for sanitation. The septic storage and pit latrine toilets are located with the vicinity of drilled boreholes. Furthermore, small scale agricultural practictice are performed which cause the use of animal manure and inorganic fertilisers. Poultry farming and ranches are most common in the study area. These has resulted in high concentration of lives stocks present in some vicinity of boreholes. Such anthropogenic activities can be considered as a source of trace metals, major anions and cations, and microbial contamination in groundwater (Mudau, 2011; Odiyo and Makungo, 2012; Odiyo et al., 2020).

1.3 Motivation

Acute water scarcity is a global problem especially in semi-arid country like South Africa. Most of the communities that depends on groundwater sources do not know the quality of water they drink as they often presume that it is of good quality, which makes people to rely greatly on it. The use of shallow groundwater source, such as hand dug wells and deep groundwater sources (boreholes) are common in South Africa (Edokpayi *et al.,* 2018b). In rural areas, schools and clinics are often not supplied with potable water and they rely solely on groundwater which are not often monitored. Groundwater can be contaminated by the ingress of human and animal waste into the aquifer (Hynds *et al.*, 2014, Sasakova et al., 2018). This could be through the grazing of animals, discharge of domestic and industrial wastewater, use of pesticides and fertilizers in agriculture (Lindgren *et al.*, 2016). The location of some of the boreholes are very close to pit latrines, graveyards and landfill sites which are potential sources of pollution. Due to the lack of data or research study on water quality status of groundwater in the selected villages, this study will fulfill the knowledge gap by monitoring the borehole in the selected villages. It is vital to monitor chemical and microbial concentration of groundwater use by people in Collins Chabane and Makhado community for various domestic and agricultural activities. Hence, this study will investigate and give baseline data of groundwater composition thereby close the information gap regarding groundwater quality of Collins Chabane and Makhado Municipality areas.

1.4. Objectives

1.4.1 Main objective

To assess the human health risk associated with the consumption of groundwater around Collins Chabane and Makhado Municipality, Vhembe district.

Specific objectives

- To assess the microbial water quality in primary schools, private household and communal boreholes located within Collins Chabane and Makhado Municipality of Vhembe district, South Africa.
- To determine the concentration of anions and metals within the selected location.
- To ascertain the suitability of water use based on water quality index
- To evaluate the geochemical characteristics of the groundwater in the study area.
- To assess potential health risks associated with the use of groundwater for domestic purposes.

1.5 Research Questions

- Which groundwater samples contain high pathogenic organisms in the study area?
- Which of the major anions and trace metals will be found in high quantity in the selected groundwater use for domestic and agricultural purposes?
- What is the suitability of groundwater in the study area?
- What is the geochemistry of groundwater in Collins Chabane and Makhado Municipality, Vhembe District, South Africa?
- Will the concentration of contaminants in the investigated groundwater samples pose any health risk for people living in Collins Chabane and Makhado Municipality, Vhembe District, South Africa?

1.6 STUDY AREA

The study area is located within Collins Chabane (546 721.572 ha; 5467.216 km^2) and Makhado (831 058.64 ha; 8310.586 km^2) local Municipality area (Bungeni, Mashau, and Masia) of Vhembe District, Limpopo province (VDM, 2021). The Municipalities are located in the Northern parts of Limpopo Province (Geological coordinates 23° 00′ 00′′ S 29°45′ 00′′ E) approximately 100 km from the Zimbabwean border along the N1 route (MNIDP, 2015). The municipal area is 8567, 38 km^2 (856 738 ha) in size and strategically located on a macro scale along a major passage between South Africa and the rest of the African continent (Stats SA, 2011).

Approximately 764 702 people currently reside within the Collins chabane (347975) and Makhado (416727) Municipality and based on the vastness of the rural populace, the municipality is classified as predominately rural (Stats SA, 2016). Figure 1.1 below is the map of the study area showing random selected sampling points.

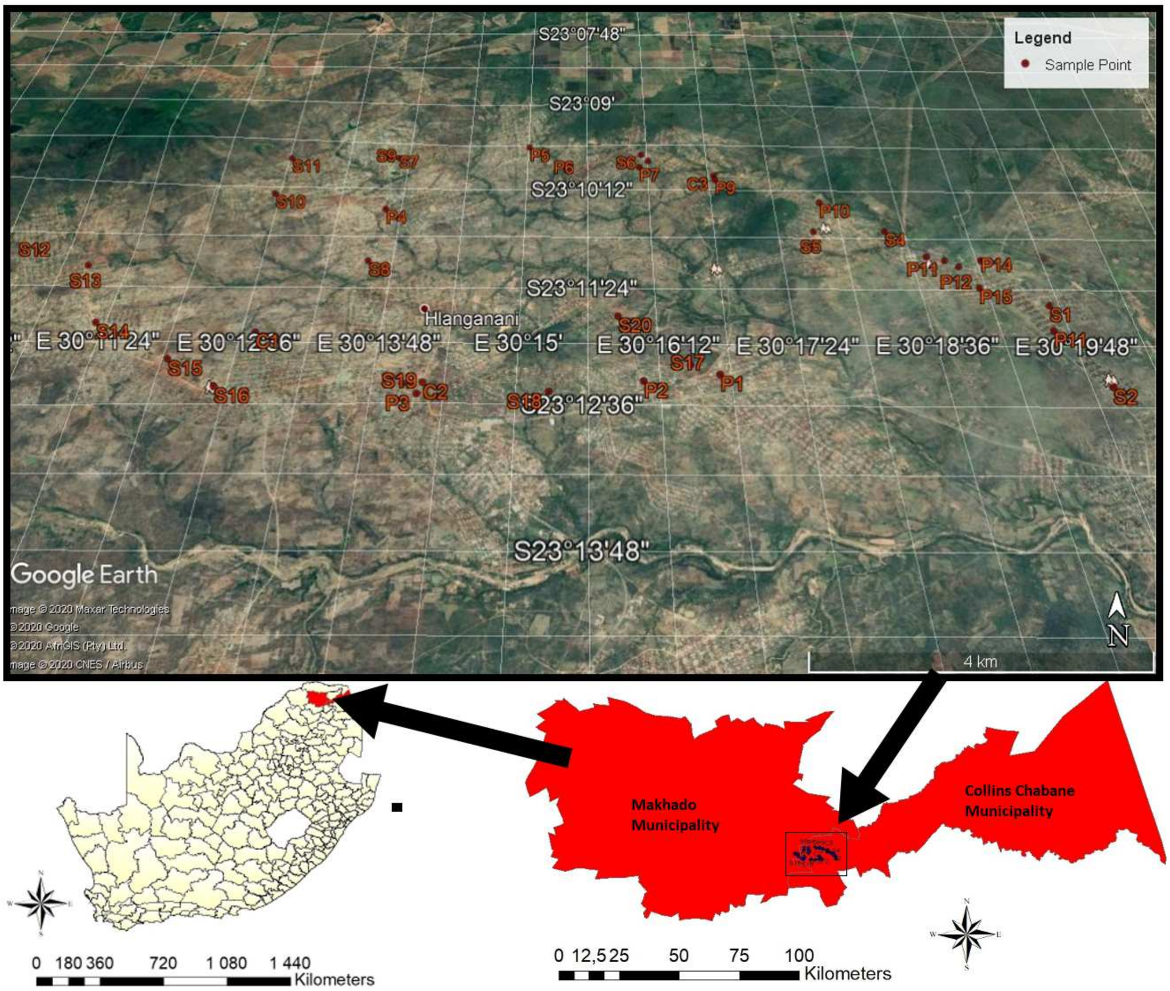

Figure 1:1 Map of the selected Collins Chabane and Makhado municipality study area.

1.6.1 Climate

The temperature of the study area ranges between 18°C in the mountainous areas to 28°C in the rest of the area, with an average of 25.5°C (MNIDP, 2015). Maximum temperatures occur during the month of January, while the minimum temperatures occur in July (Makhado Municipality IDP, 2015). The main period for rainfall is January to February with an annual rainfall of 450 mm in the low-lying plains to 2300 mm in the Soutpansberg (Makhado Municipality IDP, 2015). The general average rainfall for the Municipal area ranges between 450 mm to 800 mm (Makhado Municipality IDP, 2015).

The areas north of the Soutpansberg have less rainfall than the lower western foothills and central and eastern high lying areas of the mountain itself. Higher rainfall occurs on the higher lying areas of the Soutpansberg and foothills of the mountain (Makhado Municipality IDP, 2015).

1.6.2 Land use

The study area consisting of households, schools, crèche, churches, cultivated farms, tenant residences and hotel. It also encompasses dense bushes and trees, sewage treatment plant sites and water basins which make up a large portion of the study area. On a macro scale, the majority of established land uses within the Municipality area include: commercial, conservation, cultivated land, forestry, mining, residential, subsistence farming and large pockets of unspecified land parcels and fundamentally zoned agricultural (DWS, 2012). Large sections of the open area of both Collins Chabane and Makhado municipality are used for farming purposes. Approximately 10 478 farmlands are located in the study area (Makhado Municipality IDP, 2015). Most of the areas in-between settlements are utilised for farming purposes resulting in constant threat of environmental pollution (Makhado Municipality IDP, 2015). Some villages in the study area are classified as natural growth centres, this means the villages have larger populations with better infrastructure but not proclaimed (Makhado Municipality IDP, 2015).

1.6.3 Topography and slopes

The topography of the municipal area is characterised by a mountainous makeup. Settlements are mostly located on slopes less than 9% (1:10), many of the urbanized areas (settlements) are located between the mountainous areas with slopes between 9%-25% (Makhado Municipality IDP, 2015).

1.6.4 Geology

The study area is unique due to its geological formations (predominantly sandstone) (WHE, 2017). It has a fairly complex geology with relative high degree of minerals which are found in dusters in varying concentration (WHE, 2017). The geology of the region comprises of Archean aged and granite-green stone terrane of the northern extremity (WHE, 2017).

1.6.5 Hydrology and Geology

The study area is situated in the southernmost part of Collins Chabane on windward side of the Soutpansberg Mountain range, which influences the rainfall pattern in that area which can reach up to 2 000 mm and be as low as 340 mm (Odiyo et al., 2019). Rainfall peaks occurs during January and February. Warm wet season (WWS) (16 °C to 40 °C) and cool dry season (CDS) (12 to 22 °C) occurs from December to February and May to August, respectively. The study area often receives rainfall from October of the previous year to March of the following year which last for a period of approximately 182 days with the temperature ranging from 16 ºC to 30 ºC monthly. meanwhile the cool dry season extends from May to Aug with temperature ranging between 9ºC to 25ºC monthly (Nembudani, 2017). The study area lies within Luvuvhu and Letaba water management areas (WMA). According to the simplified geological map of the republic of South Africa and the kingdoms of Lesotho and Swaziland in 2008 displayed at 1:2,000,000 scale from council for Geoscience, the study area is dominated by quartzitic sandstone, basaltic lava and minor dolerite lithology.

CHAPTER 2: LITERATURE REVIEW

This chapter reviewed existing literature in the field of study to identify the scientific gaps in terms of data required as well as, the scale at which studies that have been carried out and which parameters were considered.

2.1 Groundwater quality

Groundwater is defined as water beneath the land surface, both from saturated and unsaturated zones. Whereas the quality of groundwater is described by the physico-chemical, biological and aesthetic properties of water which determine its suitability for a variety of uses without triggering any risk (DWAF, 1996; Brands *et al*., 2016). The absence of potable water to every household has led to the proliferation of boreholes as a result of its high demand and lucrative nature. In rural areas, boreholes are located either close to a pit toilet or downstream of soak away pits or adjoining landfills/waste dump sites (Afangideh *et al*., 2011). Contamination of groundwater with heavy metals and microorganisms is one of the most important concerns that have received attention at local, regional and global levels, because of their toxicity and negative impacts on public health (Ullah *et al.,* 2009).

The World Health Organization (WHO) has listed Cd, As, Pb, and Hg as a major public health concern (WHO, 2011). Due to that, several studies on the impacts of drinking heavy metals contaminated water (including groundwater) on human health have been conducted previously (Demir *et al*., 2015; Boateng *et al*., 2015; Elumalai *et al*., 2017; Tay *et al*., 2019). Although some metals at low concentrations (Zn, Co and Cu) are essential for normal functioning and growth of the human body (Ouyang et al., 2002), however, direct or indirect exposure to excess levels of these metals in a long run can lead to significant health risks (Enitan et al., 2018; Tay et al., 2019). Trace metals may enter a water supply by industrial and household wastes, leached from rocks and soils according to the geochemical mobility, or from acidic rain resulting in the disintegration of soils and releasing heavy metals into streams, lakes, rivers, and groundwater (Abolude *et al.,* 2009; Lenntech, 2011; Okoya *et al.,* 2011).

Groundwater contaminated sites can be restored with proper source delineation, removal, and control. These sites may require approaches that go beyond source treatment and could need additional approaches to address contaminants that potentially may not be completely remediated (Interstate Technology and Regulatory Council (ITRC), 2011).

The most common contaminant-related challenge for groundwater remedial efforts is the presence of dense non-aqueous-phase liquid (DNAPL) and whose presence does not necessarily mean that remediation is infeasible (USEPA, 1993). Furthermore, in order to provide reliable groundwater quality protection, alternative municipal solid waste (MSW) management approaches that properly treat wastes prior to disposal should be adopted (Lee *et al*., 1993).

2.2 Water Quality Parameters

Physical, chemical and microbial water quality parameters are measured to determine the physicochemical and microbial characteristics of water, thus by comparing the measured values with standard guidelines of WHO and SANS 241 (SANS, 2015; WHO, 2015). The physical properties include taste, turbidity, total suspended solids, salinity, colour and odor whereas chemical properties referred to as dissolved inorganic substances such as metals, organic chemical and some other salts. Microbial measurands characteristics in water quality matrix include faecal indicator organisms and their species with both non- and pathogenic strains, protozoa, viruses and other bacteria that can have both positive and negative health effects on aquatic and terrestrial organisms including humans (OECD, WHO, 2003; Solomon, 2008). These parameters need regularly monitoring to minimize and prevent the outbreak of waterborne diseases in both developed and developing countries.

2.3 Previous Research

Tay *et al*., (2019) indicated that, the potential non-carcinogenic risks of exposure (HQing/derm) posed by Fe, Mn, Cd, Cu, Zn, Pb, As and Hg within a single route of exposure via ingestion or dermal contact is 3.30×10^{-2}, 1.40×10^{-1}, 5.00×10^{-4}, 3.70×10^{-2}, 3.00×10^{-1}, 3.60×10^{-2}, 3.00×10^{-4} and 3.00×10^{-4} respectively for both adults and children. The risk index factor (Ri) analysis further suggests that, groundwater within the study area was potentially threatened by anthropogenic activities. Mercury, arsenic and cadmium were major contributors to the Ri. In the study conducted by Sorlini et al. (2013), water supplies were sampled from boreholes, open wells, rivers, lakes and piped waters. The waters of the Logone valley were found rich in Iron (Fe). The highest values measured in the boreholes and open dug well with concrete walls in Djougoumta and piped water in Fianga were 25.2 mg/L, 15.0 mg/L and 19.6 mg/L respectively.

About 55% of samples in the Logone valley were found with Fe concentration above 300 µg/L which may cause organoleptic problem (Hoko, 2008). 24% of the sampled sources had Mn and Pb concentrations exceeding the WHO guideline value. The maximum value of 1.5 mg/L was observed for both Mn and Pb in the borehole of Kamargui-Bosgoye (Cameroon).

Esterhuizen (2012) assessed 75 dairy farm borehole water quality in the greater Mangaung region of the Free State Province, boreholes on 22 farms (29.3%) were contaminated with *E. coli,* while 60% exceeded the prescribed SANS 241 (2015) and WHO (2008) limits for total coliform bacteria (< 10 cfu/100 mL) and *E. coli* (0 cfu/100 mL) collectively. Nine of the farm boreholes had levels of total coliforms and *E. coli* beyond the recommended SANS 241 (2015) standards. Two farms did not conform to SANS 241 (2006) standards for chemical parameters, one had high levels of Ca, Mg, Cl and N while the other farm exceeded the levels of Mg, Na, F, Cl, and N. Faruque, et al. (2002) investigated two major rivers and a lake in Dhaka City for the presence of Shigella-specific virulence genes such as ipaBCD, ipaH, and stx1 using PCR assays. One or more of these virulence genes were detected in the boreholes investigated with isolates that shared ribotypes with clinical isolates.

Bessong *et al.* (2009) conducted a study in Tshikuwi Community in Venda, South Africa from two groundwater storage tanks (Tank 1 and Tank 2) and the Khandanama River. Microbial counts for total coliforms, faecal coliforms, enterococci, and heterotrophic bacteria from Tank 1 and the Khandanama River sample exceeded the limit for SANS guidelines for domestic use. Of the 40% (n=354) of the households investigated, (42% and 34% of individuals who used tank 1 and 2 had diarrhea, respectively. Outbreaks of diarrhea in Republic of South Africa have been previously reported in KwaZulu-Natal, Gauteng and Mpumalanga province due to the contamination of rural water sources by Shigella dysenteriae type 1 and *Vibrio cholerae* O1 biotype El Tor, respectively (Morgan, *et al*., 2007; Pegram *et al.,* 1998).

Several studies had detected high nitrate concentrations from borehole samples collected from primary school in South Africa which exceeded the standard guidelines (Samie et al., 2011; Akwensioge, 2012; Samie et al., 2013; Odiyo et al., 2020). High fluoride concentration were detected in groundwater samples collected from primary school in Siloam Village, South Africa which cause 50% of learners to suffer mottled teeth (Odiyo and Makungo, 2012).

A maximum enumeration level of 130 and 219 cfu/100 mL of E.*coli* and total coliform were recorded in Siloam Village, South Africa by Odiyo and Makungo (2018) which suggest high risk of infectious disease transmission. High values of physico-chemical parameters such as turbidity (11.85NTU), EC (139.9mS/m), pH (9.28) and major metals and non-metals (mg/L) such as F, Cl, Sulphate, Nitrate, Mn and Fe were also recorded with high values of 5.89, 410.86, 404.01, 543.27, 0.23 and 0.17, respectively which exceeded the DWAF (1996) guideline for domestic water use in wet season. Most schools in Vhuronga 1, Limpopo Province, South Africa had high annual risks of infection due to Shigella flexneri and E. coli with maximum values of 83.75 and 89.11% respectively (Odiyo et al 2020). Molekoa et al. (2019) conducted a hydrogeochemical assessment of groundwater quality of Mokopane Area, Limpopo, South Africa which was achieved through plotting of major cations and anions in the Piper diagram. The diagram suggested that water samples falls under Na-Cl (8%), Mg-HCO_3 (42%) and Na-HCO_3, (50%), water type.

2.4 Physico-chemical parameters

These sections entails the details of the parameters that affect groundwater quality. These properties can be physical or chemical. Physical properties of water quality include temperature and turbidity while chemical characteristics include parameters such as pH and electrical conductivity (EC), total dissolved solids (TDS) and dissolved oxygen (DO). Groundwater quality monitoring assist researchers to predict and learn from natural processes that take place in the environment and determine the level of human impacts on the ecosystem and geology (Water Quality, 2021). The analysed results of physico-chemical parameters are useful in ecological restoration projects. The most common physico-chemical parameters of interest in drinking water are pH, TDS, salinity, temperature, alkalinity, complete hardness, turbidity, TDS and EC. Such standards are used for aesthetic properties, rather than health concern. The aesthetic properties of water can be determined by contact, vision, smell and taste. For instance, color, turbidity, floating debris, sight-suspended solids, touch-by-touch temperature smell taste and odor. The temperature of water has a certain impact on the physical properties of water such as viscosity, dissolved gas solubility, salinity, etc. (Chirag, 2017). The rate of water reactions rises as the temperature rises.

Electrical Conductivity (EC) is the water metric for conducting measured electrical current in mS/m. The EC correlate with other parameters such as pH, TDS, salinity, temperature, alkalinity, complete hardness, other ions such as calcium (Ca^{2+}) and bicarbonate (HCO_3^-), etc.

High conductivity in groundwater influence water to be more corrosive which affect the taste and odor of water quality sensitivities for humans (Patil *et al*., 2012). Materials that passed straight into water, such as debris, sewage effluent, storm runoff particles, etc., are sources of flavour and compounds that changes the odors of water (Fondriest Environmental, 2013).

Turbidity in water is the determination of water's clarity (EPA, 2012). Turbidity is used as reflection to the possibilities of the presence of microorganisms that may cause diseases, making water aesthetically unattractive (Fondriest Environmental, 2013). Ground water contaminated with high elevation of TDS may cause gastrointestinal irritation and unwanted taste (Chirag, 2017). Water can be classified as acidic, neutral or alkaline by determining the level of potential hydrogen ions concentration in water. Alkalinity and pH are crucial water quality parameters. Changes in pH and alkalinity level cause water to taste bitter, be corrosive and can affect the solubility and toxicity of heavy metals in the water (DWAF, 1996; USGS, 2013). Alkalinity and pH parameters play a major role in water supply systems as they influence disinfection, corrosion control in water distribution pipe networks and softening processes (Nanyang Technological University, 2004).

Water hardness is generally described as a measure of the capacity of water to react with soa., Water hardness is caused by a variety of dissolved polyvalent metallic ions, predominantly calcium and magnesium cations. These two principal ions are commonly sourced from sedimentary rocks (mostly being limestone and chalk), seepage and runoff from soils (WHO, 2011). Both calcium and magnesium are vital minerals to human health. Inadequate intakes of calcium have been associated with increased risks of nephrolithiasis (kidney stones), colorectal cancer, hypertension and stroke, and obesity. However, high level of complete hardness cause unpleasant taste and stain clothes (Edokpayi et al., 2018a). Water with total hardness of < 60 mg/L, 60 mg/L to < 120 mg/L, 120 to < 180 mg/L and ≥ 180 mg/L is categorised as soft, Medium hard, hard and very hard, respectively (British Colombia, 2007b, WHO, 2011). Groundwater associated with a hardness level beyond 200 mg/L could cause scale deposition in water supply distribution pipes and storage tank. On heating elements or containers such as electric kettle and geysers, hard waters could form deposits of calcium carbonate scales (WHO, 2011; Edokpayi et al., 2018a).

2.4.1 Trace metals

Trace metals occur naturally in low concentrations. However, geological and anthropogenic activities (combustion of fossil fuels, chemical industry, pesticides, mineral fertilizers and herbicides) lead to increase in their concentrations, which makes metals such as mercury (Hg), Cadmium (Cd), Arsenic (As), Lead (Pb), Chromium (Cr) dangerous to both human health and the environment (Maurya *et al*., 2018; Lin *et al*., 2018). Metals such as selenium (Se), Aluminum (Al), Gold (Au), Iron (Fe), Zinc (Zn), As are used as food supplement, and remedies for anti-acids, rheumatoid arthritis, anemia, leukemia and homeopathic medications (WHO, 2011). Hence, some of these metals such as cobalt (Co), Copper (Cu), Cr and Nickel (Ni) are necessary for humans' body in small quantity while others are carcinogenic, which affect, among others, the central nervous system (Hg, Pb, As), or skin, bones, or teeth (Ni, Cd, Cu, Cr) and or liver, the kidneys (Pb, Hg, Cd, Cu) while, Zn and Pb can cause corrosion (WHO, 2011).

2.4.2 Major anions

The SANS 241 of 2015 has listed chloride, sulphate, carbonates, fluorides, and nitrate as major ions of interest for drinking water standard as they are essential in the carbonate system, which provide natural water buffer capacity and is responsible for the alkalinity of water. These ions are produced naturally in geological formations such as magmatic rock formations, deposition of salts and weathering (Chirag, 2017; Barbieri *et al*., 2019). Though these anions occurs naturally, excessive amount of their concentration are found in groundwater due to the geologic unit, physiological conditions of rock and rock geochemistry (Wu *et al*., 2016). However, anthropogenic sources, such as run-off containing road de-icing salts, landfill leachates, the use of inorganic fertilizers, septic tank effluents, industrial effluents, animal feeds, irrigation drainage, and extensive use of groundwater also contribute to their excessive amount in groundwater when surface water interact with groundwater (Mukherjeea, and Singh, 2020).

Drinking water with excessive amount of these chemical can cause skeletal and dental fluorosis (F^-), hypertension (Cl^-), methaemoglobinaemia (NO_3^-) etc. (DWAF, 1996; Topal *et al*., 2012; Chirag, 2017). An increase in sulphate and chloride concentrations causes change in some physical properties of water such as noticeable taste, smell, and can have a negative impact on human health (Ghosh *et al*., 2013; WHO, 2017).

Moreover, fluoride pollution in groundwater is considered a universal problem and it is reported that two hundred million people from different countries (25) which include West and Southern Africa, China, India, Mexico, Iran, Pakistan, Sri Lanka and Thailand are threatened and affected by incident of dental fluorosis (Malago, 2017; Rasool, *et al*., 2018).

2.4.3 Major cations

Major cations in natural water include calcium, magnesium, sodium and potassium (Parikh et al., 2012). These cations occur naturally in ground water in fluoride bearing minerals such as fluorapatite [$Ca_5(PO_4)_3F$], fluorite (CaF_2), sellaite (MgF_2), amphiboles, micas and cryolite (Na_3AlF_6) are found in the igneous rocks (such as gneisses, granite, and pegmatite) and sediments (Vithanage and Bhattacharya, 2015). Hydrolysis reactions of halite and calcite, silicate, micas such as biotite and muscovite could lead to concurrent release of fluoride, sodium and potassium ions ((Mukherjeea, and Singh, 2020). Sodium ($NaHCO_3$) and magnesium ($C_2H_2MgO_6$) are used as remedies to fight cancer, sodium bicarbonate can rapidly alkalise the human body effectively than diet. However, excess amount of sodium in the human body has adverse human health (Lee *et al*., 2012; Sircus, Mark, 2019). Excess concentrations of sodium give rise to unacceptable taste in drinking water (WHO, 2011).

Calcium is the most predominant water cation which is also classified as the major component of water hardness. Excessive accumulation of calcium carbonate in related piping, and heat exchanges, affect heat transfer and warm water heaters, boilers which may result in the piping being plugged. Meanwhile in iron and steel tube, it precipitates as calcium carbonate which assist to prevent corrosion (WHO, 2011). Potassium (K) plays an important role at the cellular level (Tetzlaff, 1993). It also assists in the heart and skeletal muscle contraction, glomerulo-tubular renal function and nerve conduction. Low or high concentrations of K can lead to potentially fatal problems in excitatory tissue, mainly the cardiac muscle (Parikh et al., 2012).

2.5 Microbial contaminants

The following microbial parameters are most important indicator species commonly found in contaminated fresh and groundwater that causes waterborne diseases.

2.5.1 Total coliform

Total coliforms are a group of bacteria which share common characteristics in nature (Zucker, 2017). Most members of the total group of coliforms are found in the water influenced by surface water, human or animal waste, soil and submerged wood (WHO, 2011).

Some particular groups of these bacteria are excreted in the animal and human wastes, but most of coliforms are heterotrophic and able to reproduce in water and soil environments (WHO, 2011). The effectiveness of total coliform as an indicator of fecal contamination is determined by the extent to which species of bacteria found originate from fecal and human waste. The analysis of total coliform remains fundamental in standard drinking water test, since its presence designates contamination of a water supply by external sources (EPA, 2006). According to SANS 241, the recommended standard of total coliforms is 10 cfu/100 ml (SANS, 2015).

2.5.2 Escherichia coli

Escherichia coli (E. *coli*) is considered the major species indicator of fecal contamination and occurs in elevation numbers in human and animal wastes, sewage and water subject to recent fecal pollution (WHO, 2011). *Escherichia coli* is the major species in the fecal coliform group. In comparison to the five general groups that involve total coliform, only E. *coli* does not grow and replicate in the environment in nature. Consequently, E. *coli* species is considered the best indicator of fecal pollution and the possible presence of pathogens (disease-causing organisms) since it can be easily grown in the laboratory and assessed for water quality. Its presence in a water sample indicates the presence of sewage material that may cause pathogens, such as *Vibrio cholera*, which causes cholera (American Well Owner, 2002). Drinking water contaminated with *E. coli* may result in diseases such as cholera, diarrhea etc. (WHO, 1993). According to SANS 241 (2015) and WHO (2015), the recommended standard of E. *coli* is 0 cfu/100 ml.

2.6 Groundwater pollution in South Africa

There have been reports of acid mine drainage (AMD) pollution on water resources and the environment from coal mines in Mpumalanga and from gold mines in Johannesburg (DWAF, 2010). Residents of Carolina, a town about 270 km from Johannesburg have been exposed to water contaminated by AMD (Kings, 2012). Improper sanitation in several informal settlements in Johannesburg has resulted in groundwater pollution (Kunene, 2009). The Crocodile River in Limpopo has also been polluted by AMD and radioactive sludge from the West Rand mines (FarmiTracker, 2010). The Vaal River has also been polluted by municipal effluent as well (McCarthy and Venter, 2006).

From 1993 to 2007, there were outbreaks of diarrhea and typhoid in Delmas, a town in the Mpumalanga Province (Nealer *et al.,* 2009). Studies disclosed that groundwater abstraction boreholes located downstream of wastewater treatment facility were contaminated by the effluent from the treatment facility (Nealer *et al.,* 2009) likewise mining activity also have great impact on groundwater resources (GDAEC, 2008).

2.6.1 Sources of ground water contamination

Ground water are prone to contamination from natural and anthropogenic sources. Residential, municipal, commercial, industrial, and agricultural activities can all affect ground water quality. Contaminants may reach ground water from activities on the land surface, such as releases or spills from stored industrial wastes; from sources below the land surface but above the water table, such as septic systems or leaking underground petroleum storage systems; from structures beneath the water table, such as wells; or from contaminated recharge water (ARGOSS, 2001).

a) Natural Sources

Several contaminants dissolved in groundwater such as iron, manganese, arsenate, chlorides, fluorides, sulfates, or radionuclides occur naturally in geological materials such as rocks or soils (Sharma and Bhattacharya, 2017). Other naturally occurring substances, such as decaying organic matter can move into groundwater as particles (EPA, 1993). Groundwater with unacceptable concentrations of these substances is not supposed to be used for consumption or other domestic water uses unless it is treated to remove these contaminants (EPA, 1993; Ghrefat et al., 2014).

b) Anthropogenic sources

These are threats to groundwater quality due to contamination from agricultural wastes, spillage, leaking of underground storage tanks and septic systems, urban runoff, industrial and mining operations (ssaracino and Phipps, 2002).

i) Burial sites

Pathogens (germs and viruses) from decomposing corpses can move through the soil and they can survive in the soil for many days. Infiltration from burial site via rainfall runoff can transport pathogens into groundwater.

As water infiltrate the soils in cemeteries, both chemical and biological contaminants could be leached and percolates groundwater, hence reduce its water quality (William *et al*., 1992). Sadly, groundwater pollution of cemeteries has largely been overlooked in South Africa (Engelbrecht, 1998).

ii) Informal vehicle servicing, spray painting and parts washing facilities

The risk of groundwater contamination depends on the type of liquid and the amount spilled or disposed of soil types, amongst other factors (DWAF, 1998). In cases where borehole/well pumps are equipped with engines, a potential groundwater contamination may occur. When used fuel, brake fluid, oil, paint residues, radiator water, solvents, cleaning fluids or used wash-water are disposed of, or spilled, onto the ground in the immediate vicinity of the borehole or well pollute groundwater (DWAF, 1998).

iii) Sanitation facilities

ARGOSS (2001) describe that almost all systems of sanitation represent a possible source of faecal pollution. In urban areas, leaking sewers may add to substantial microbiological and nitrate loads to shallow aquifers that may affect groundwater supplies used for drinking purposes (ARGOSS, 2001). Water resources can be contaminated both directly and indirectly by the disposal of excreta in a rural environment. Germs, viruses and other substances from excreta in pit latrines can move through the sub-surface soils and contaminate groundwater. The risk of groundwater being contaminated by pit latrines is increased where high loading occurs due to more people relying on pit latrine toilet (DWAF, 1994).

Wastes from septic tanks, cesspools, privies and septic systems that are improperly sited, designed, constructed, or maintained can contaminate groundwater with bacteria, viruses, nitrates, oils, detergents and chemicals (USEPA, 1999). According to Collins Chabane Local municipality IDP of 2017/18, wastewater plants receiving more inflow than the design capacity; vandalism and theft of manhole covers and cables; introduction of undesirable objects in the sewerage system, lack of staffing to operate the plant, deterioration of infrastructure, overgrown shrubs and grass at plants and poor maintenance of sewerage system and lastly centralisation of workers may result in poor sanitation (Edokpayi et al., 2020).

iv) Disposed waste into standing water

Discarding of waste from many households directly into standing water bodies may leach into the ground which may contaminate groundwater (USEPA, 2015). Leachate can also flow directly overland into surface water resources or move through soils and enter groundwater resources (Ololade et al., 2019). If water is contaminated by leachate, the taste and odour of the water can be objectionable. Pathogens and potentially toxic trace elements from leachate pose a health risk if the water is used for drinking purposes (Ololade et al., 2019).

2.7 Groundwater utilization in South Africa

Groundwater is widely but variably used in South Africa and it constitutes 15% of overall water consumption. A greater proportion (64%) of the total groundwater extracted is used for irrigation purposes (Woodford *et al.,* 2009) with a high extraction and dependence as main source of water in the rural areas (Tewari and Kushwaha, 2008). Anthropogenic practices such as mining, agriculture, sanitation and industrial activities are negatively affecting the resource and thus, threatening water security of South Africa (Molobela and Sinha, 2011; Edokpayi et al., 2017).

2.8 Groundwater recharge in South Africa

UNESCO (2003) defined groundwater recharge as the process whereby an addition of water to a groundwater reservoir is taking place. Groundwater is recharged through downward movement of water through the unsaturated zone into the water table; “Lateral and/or vertical inter-aquifer flow; induced recharge from nearby surface water bodies resulting from groundwater abstraction; and artificial recharge such as from borehole injection or man-made infiltration ponds” (UNESCO, 2003). Factors affecting recharge include climate, type and amount of vegetation cover, types of land use, topography, nature and geometry of aquifers in the catchment, residual soil moisture retained in the soil profile from previous rainfall events” (Anaman, 2013). Sub-urbanization and urban sprawl contribute to low levels of groundwater recharge (Ruohong, 2009; McGuffin, 2012). Many cities, especially the primary cities of South Africa are faced with the problem of sprawl as a result of an increase in the number of people moving into the cities and town (Burak Güneralp et al., 2017). Urbanization increases hard surfaces such as parking lots, streets, driveways, buildings, etc on land. These surfaces are non-porous which result in an increase of water runoff into surface water bodies rather than water infiltration as a natural process for groundwater recharge (McGuffin, 2012; Scott, 2016).

Agricultural industry is another sector linked to groundwater usage. The sector is the single major user of water (including groundwater) in South Africa. It is estimated that about 78% of all groundwater abstracted is used for irrigation (Pietersen et al., 2011). The introduction of central pivot irrigation systems has led to substantial use of groundwater resources in the country which resulting in a negative water balance (Zahn and Conrad, 2009). The use of pesticides, fertilizers, herbicides and growth hormones are contributing to groundwater quality complications, specifically diffuse pollution. Nitrate is the most common agricultural contaminant (Pietersen *et al.,* 2011). Salinization of groundwater is taking place beneath lands that are exposed to extensive irrigation (Pietersen *et al.,* 2011).

2.9 Methods of Evaluating Trace Metals, Anions and Microbes in Groundwater

2.9.1 Technical application for Cation and Anion analysis

Several methods exist for analysing anion and cation concentrations in water samples. The method used depend on element of interest and the accuracy of the results, cost, the ability to detect ions rapidly and sample throughput. Several studies present various methods used for the characterisation of groundwater. The commonly used method is inductively coupled plasma optical emission spectrometry (ICP-AES/ICP-OES) which has been used in several studies such as Vetrimurugan et al. (2017), Edokpayi at al. (2018b), Moldovan et al. (2020) among others. In the last decades, the method of ICP-AES has become very popular due to the advantages of being sensitive and is an overall multi-element atomic spectroscopy technique. Analytical advantages of the ICP-AES over other techniques, such as flame atomic absorption spectrometry (FAAS), include the multi-element analysis capability of ICP-AES, coupled with its high sensitivity; the large dynamic linear range of detection; the reduction of matrix interferences and enhanced productivity (Hill, 2007). However, its detection limit is moderate to low if compared to inductively coupled plasma mass spectrometry (ICP-MS). The downside of ICP-MS is the requirement of high initial capital and cost of maintenance (Jajda et al., 2015).

(i) Ion chromatography

Ion chromatography (IC) is used for analysis of cations and anions in aqueous samples (Joachim *et al*., 2004). Ion chromatography is a form of liquid chromatography in which the mobile phase is liquid and stationary phase is solid. Liquid chromatography uses ion-exchange resins to separate atomic or molecular ion and non-volatile compounds e.g., pesticides and proteins (Environmental Protection Agency (EPA), 2007). This technique can provide quantitative analysis of anions in part per billion (ppb) (Joachim *et al.,* 2004). (Joachin et al., 2004).

The IC is typically used for the determination of anionic analytes in aqueous samples due to its better accuracy if compared to Ailzari visual methods and Ion selective electrode technique (Joachin et al., 2004). According to EPA (2007), Ion chromatograph is able to measure major anion concentrations such as F^-, Cl, NO_3^-, NO_2, and SO_4^{2-} and some cations such as Li, Na, ammonium, K, Ca, and Mg. The advantage of IC is the ability to measure concentration in parts-per-billion (ppm) range and possible determination of simultaneous ions in a short time, good reproducibility of results and high sensitivity (Peter, 2000). The drawback of this equipment lies in the blockage of pipes which could interfere with the analytical results especially if there are some particles mixed with water (Peter, 2000).

(ii) Inductively coupled plasma-optical emission spectrometry (ICP-OES)

ICP-OES is an atomic spectroscopy which has been extensively in inorganic chemistry to analyse total element concentrations in several sample types, and generally permits rapid sample throughput (5-30 elements per minute) (Tyler et al., 2002). This optical technique is capable of detecting atomic concentrations up to sub ng/ml levels (in water samples of a few millilitres or less. Furthermore, it allows for isotope-specific measurements in simple form. The ICP is a stable argon plasma heated by inductive coupling of argon cations and free electrons. Plasma's temperature range between 6–7000°K. Water samples are nebulized (at about 0.4 ml min−1 solution consumption) to produce an aerosol of fine droplets whereby spray chamber specifically select smallest droplets for analysis which mostly are approximately less than 5 microns (Mudalige et al., 2019). The selected droplets are swept into the centre of the plasma by an argon stream. Argon streams sweep selected droplets into plasma (centre) to undergo rapid heating to dissolve droplets, and then breakage molecular bonds. As a resulting, free atoms get excited with many being ionized. As atoms leave the plasma and cool, they relax which leads to emission of light which is then detect (Vlado Valković, 2000).

ICP-OES detection limit for various elements range between 1–100 ng/ml (ppb) in solution. A few elements, particularly Be, Li, Ca, Mg, Ti, Sc, Sr, µn, Y, Sr, Cu and Ba, have < 1 ng/ml detection limit. In comparison with other technique such as ICP-MS, ICP-OES is less sensitive (by 1–3 orders of magnitude) and fails to offer isotope specific information (Vlado Valković, 2000). Apart for it having good properties such as multi-element, high productivity, robust interface, excellent screening abilities and economical for many samples and/or elements, the technique has downsides: spectral interference is possible including moderate to low detection limit depending on other elements present. In this regard, ICP-OES has improved if compared to FAAS (Thermo Elemental, 2001; Nazarenko, 2004, EPA, 2007).

(iii) Capillary electrophoresis (CE)

Capillary electrophoresis (CE) refers to the electrophoretic separation of ions dissolved or suspended in an electrolyte. Samples are introduced into a capillary tube containing an electrolytic buffer. Under the application of an electric field the cations in the sample migrate toward the negatively charged electrode (cathode) and the anions migrate toward the positively charged electrode (anode). This technique may be coupled with a variety of determinative techniques for quantitative analysis. Interestingly, inorganic anions in environmental samples can be measured using CE (EPA, 2007).

(iv) Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS is highly sensitive and capable of determining wide range of metals and some non-metals at concentrations below one part in 10^{12} which is not possible with other techniques (Howard, 2000; Shimizu et al., 2006; Boutakhrit et al., 2010). ICP-MS is a multi-element system that likewise uses an ICP plasma source to separate the sample into its constituent atoms or ions. In that case, the ions are detected, instead of the light they emit (Thermo Elemental, 2001). An ICP-MS system is also capable of monitoring isotopic speciation for ions of choice (Howard, 2000). An ICP-MS have excellent detection limit for most element with the ability to analyse all sample in less than a minute in the region of nanograms per litre to 10 or 100 mL per litre or around 8 orders of magnitude of concentration units (Howard, 2000). Spectral interference problems in ICP-MS are few and but well-documented (Thermo Elemental, 2001).

Most ICP instruments limit the sample TDS level to approximately 0.1 to 0.2 percent salts by weight. Higher salt contents can enhance atomization and ionization of some elements and suppress or interfere with others (Lynch and Walsh, 1997). In comparison with other technique (AES, GFAA or FLAA), ICP-MS process multi-element with excellent detection limits and high productivity. It is inexpensive for several samples and/or elements. (Thermo Elemental, 2001). The greatest disadvantage of ICP-MS is isobaric elemental interferences caused by different elements forming atomic ions with the same nominal mass-to-charge ratio. Mathematical correction for interfering ions can minimize these interferences (EPA, 2007). Furthermore, some of its method need a developed skill person and need higher initial capital to operate use (Thermo Elemental, 2001, Jajda et al., 2015).

2.9.2 Human Health Risk Assessment

The exposure pathways of the metals in water include direct ingestion and dermal contact, but the later can be negligible in comparison to oral intake. The daily exposure for ingestion route can be determined from modified equations of USEPA (1989); De Miguel *et al.* (2007) and also Kici´nska and Mamak (2017). Human health risk assessment (HHRA) also includes estimation of the nature and magnitude of adverse health effects in humans who may be exposed to hazards in contaminated environmental media. Risk assessments consist of hazard identification, exposure assessment, dose-response (toxicity) and risk characterization (Adamu *et al.,* 2015). The health risk assessment of each potentially toxic heavy metals is based on the quantification of the risk level and expressed in terms of cancer and non-cancer health risks (Sun *et al*., 2015). There are two toxicity risk indices which are mostly reported known as cancer slope factor (CSF) for cancer risk characterization and the oral reference dose (RfD) for non-cancer risk characterization (Adamu *et al.,* 2015; Kamunda et al., 2016). As referred from USEPA (1989), animal studies have been conducted to achieve derivation of RfD values. The animal studies were achieved through application of the "No observable effect level" principle. The application for RfD values on humans were achieved by multiplication of 10-fold to account for uncertainties (USEPA, 1989). The risk characterisation forecast on the possible cancerous and non-cancerous health risk of adults and children in the study area by assimilating all the information gathered to attain at quantitative estimates of cancer risk and hazard indices (USEPA, 2004).

Furthermore, Health risk assessment is also vital in identification of risk of infection and illness of individual due to consumption of groundwater associated with microbial contamination (Odiyo et al., 2020). These assessments provide useful data to authorities and assist in creation of groundwater resource management awareness specially in an area with blank information based on these aspects of risks of infection and illness. The are several approaches for quantifying microbial risks such as Sanitary inspection (with water quality surveillance), Risk matrices, epidemiological approach, quantitative microbial risk assessment (QMRA) among others (WHO, 2016; John et al., 2021). However, QMRA and epidemiological approaches are the most commonly used method for quantifying microbial risks in drinking water (John et al., 2021).

The QMRA clearly defines the source of faecal pollution, the presence and nature of pathogens, the routes of exposure of humans/ etiological agent and exposure outcomes; while the epidemiological approach informs the propensity of these factors implicitly (Whelan et al., 2014; WHO, 2016).

QMRA has been embedded in the WHO water-related guidelines, it provides detailed interpretation as compared to the epidemiological results through generating the estimate of human-health risk, which is not feasible with epidemiological study (Pruss et al., 2002; Whelan et al., 2014; WHO, 2016).

Furthermore, several studies over the world (i.e., Rodriguez-Alvarez et al., 2015 (Agentina), Murphy, 2015 (Canada), Ahmed et al., 2020 (Pakistan), Odiyo et al., 2020 (South Africa), John et al., 2021 (Nigeria) investigated the use of QMRA in estimating the possible health risk associated with the use and consumption of surface and groundwater for ingestion and other domestic purpose in several location such as household, primary school, among others. Four set of data (namely, hazard identification; dose response; exposure assessment; and risk characterisation and management) has been used by several studies to evaluate possible risk (Rodriguez-Alvarez et al., 2015; Murphy, 2015; Eregno, 2017; Ahmed et al., 2020; Odiyo et al., 2020; John et al., 2021).

Currently there is only a few QMRA of groundwater studies been conducted as compared to surface and wastewater (Ahmed et al., 2020; Odiyo et al., 2020; Owens et al., 2020). Several studies such as Dahlström (2011), Machdar et al. (2013), Rodriguez-Alvarez et al. (2015), Briggs et al. (2018), Ahmed et al. (2020), Masciopinto et al. (2020), among others have determined the microbial health risk using several pathogens including the including the common pathogenic strains which include Escherichia coli (E. *coli*), *Camplyobacter* spp., *Cryptosporidium* spp., *Enterococci* spp., *Salmonella* spp , *Shigella* spp , *Giardia* spp among others. These pathogens strains have been found in groundwater tested in different parts of the world (such as Pakistan Argentina, Italy, Sweden, Nigeria and Ghana).

2.9.3 Detection and Analysis of Microbial Composition in Environmental Samples

Traditional and standard analysis for the presence of microorganisms relies on the enrichment and isolation of presumptive colonies of bacteria on agar media using approved diagnostic artificial media techniques like spread or pour plate methods. This is generally followed by biochemical and/or serological identification. Traditional methods of detection, although reliable and efficient, require several days to weeks before results are produced. Furthermore, phenotypic properties by which the bacteria are identified may not be always expressed; and when expressed, they may be difficult to interpret and classify (Washington, 1996).

Recently, there has been a trend towards using Escherichia Coli to monitor the quality of final effluent prior to discharge into the environment. For microbial indicator such as E. coli and total coliform detection in water, standardized protocol and regulated conventional methods are applied (Carrillo-Gómez et al., 2019). These methods are grounded on the cultivation of bacteria which is achieved through membrane filtration, fermentation of several tubes among others (Rompré et al., 2002; Deshmukh, 2016; Carrillo-Gómez et al., 2019). Membrane filtration is feasibly the most preferred technique for the enumeration of coliforms in drinking water due to its practicality and simplicity. The preparation time of media to culture bacteria is also a critical limitation. Due to this, Hach Company has developed an alternative membrane filtration method which detect total coliform bacteria and E. *coli*. Using m-ColiBlue24® which does not require media preparation. This method differentiate E. *coli* from other total coliform bacteria based on the formation of a blue-coloured colony after a specific temperature and period of incubation. There are two different formats of m-ColiBlue24®, a broth and an agar format. Smith (2001) compared m-ColiBlue24® broth with both m-TEC agar and m-FC broth. Smith (2001) discovered that m-ColiBlue24® broth is a rapid and reliable method. Although these techniques achieve same purpose, the prolonged incubation time (at least 24–28 h) for the final detection of E. coli and total coliform is the critical limitation (Niemi et al., 2001; Mendes and Domingues, 2015, Carrillo-Gómez et al., 2019).

2.9.4 Hydrochemical and Geochemical Plots

(a) Piper and ternary diagram

Piper trilinear diagram is a hydrogeological tool applied to visualise the most dominant major ions in control of the ground and surface water chemistry of an area. Piper trilinear diagram (Piper, 1944) evaluates the evolution of the water and correlation among rock types and water composition (Ravikumar *et al*., 2015). Major cations and anions are plotted in ternary triangles as shown in Figure 2.1. The apexes of the cation triangle consist of Na^+ K and Mg, Ca meanwhile, the apexes of the anion triangle contain of SO_4^{2-}, Cl^- and HCO_3^-, CO_3^{2-}. The anion and cation ternary plots are projected into a centrally placed diamond which identify the dominant water chemistry as shown in Figure 2.1 .

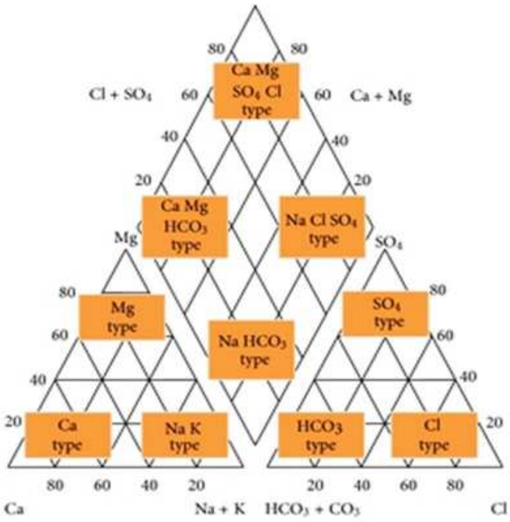

Figure 2.1: Piper plot diagram presenting water type (Piper, 1944; Al Farraj *et al*, 2012)

(b) Gibbs Diagram

The Gibbs diagram representing the boomerang contour has also been useful in groundwater hydrochemistry. Approximately 53 percent of all publications quoting the Gibbs diagram (382 out of 720) include the keyword “groundwater” (Marandi and Shand, 2017). Based on an enquiry made from the Web of Science database in year 2017, seventy two percent of these citations in (29 out of 40) focused much on groundwater chemistry which evident that this method is still effective and recommended (Web of Science, 2017; Marandi and Shand, 2017). The Gibbs diagram fails to provide information to estimate processes impacting groundwater SO4 concentrations such as pyrite oxidation (Shand et al., 2016) or gypsum dissolution (Woldemariyam and Ayenew, 2016), which can be crucial to groundwater major element compositions. The evolution of groundwater quality in carbonate aquifers was presented in Hanshaw and Back (1979), whereby these processes were described using a Piper (1944) diagram. Gibbs plot is tool used to elucidate the natural processes of evaporation-crystallization, rock-water interaction/weathering and atmospheric precipitation (Gibbs, 1970). The Gibbs diagram can also be used to show the dominant factors governing the mineralisation of groundwater. Figure 2.2 illustrate the Gibbs diagram showing groundwater mineralisation (Fig. 2.2).

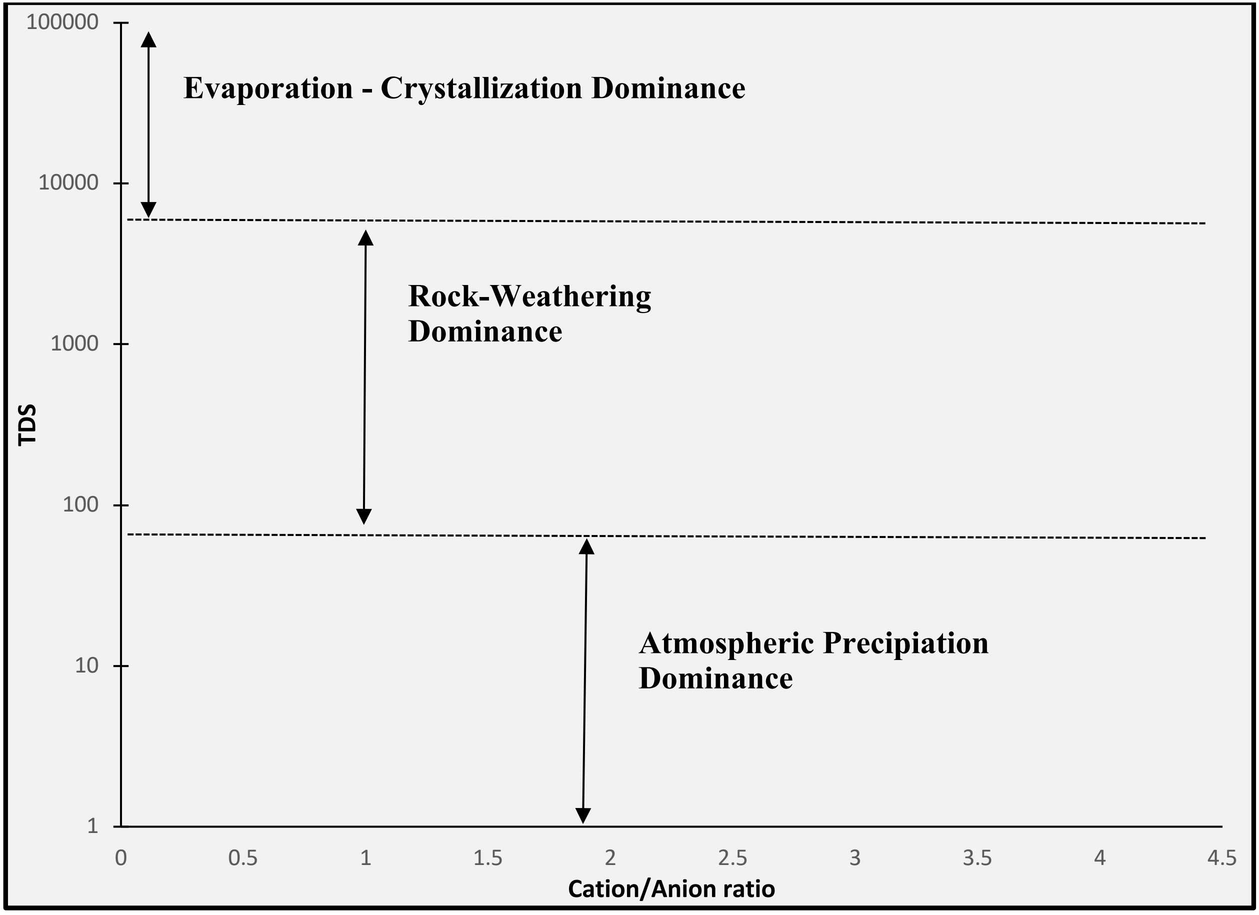

Figure 2.2: The Gibbs diagram modified after Gibbs (1970).

2.9.5 Water quality index (WQI)

Water quality indices (WQI) is the principal parameter used to determine groundwater quality and its aptness for human consumption (Mishra and Patel, 2001; Avvannavar and Shrihari, 2008). This concept is constructed on the contrast of the water quality parameter (physical, chemical and microbial parameters) with respect to regulatory standards (Khan et al., 2003). This is a technique of ranking that offers a joint control of most important water quality parameters on the overall excellence of water for human consumption (Singh et al., 2016). Water quality indices evaluate the aptness of the excellence of the groundwater for different uses (Cude, 2001). The application of WQI technique makes it simpler to present results of an investigation (related to a water body), as it gives a summary of analysed parameters in one value for each sample (Couillard and Lefebvre, 1985; Tiwari and Mishra, 1985; Almeida and Schwarzbold, 2003; Liou et al., 2004; Dwivedi and Pathak, 2007).

Indices are used in monitoring programs that assess ecosystem health (Garcia et al., 2018). These techniques assist the decision-makers, general public and potential stakeholders about the present state of the ecosystem (Nasirian, 2007; Simoes et al., 2008). Likewise, WQI offers a standard method for assessing achievements and failures of management strategies which can be used in improving water quality (Rickwood and Carr (2009). This index is a numeric expression used to summarise huge number of variables data into a single number, hence, represents the water quality level (Miller et al., 1986; Bordalo et al., 2006; Sanchez et al., 2007). The assigned weight of a parameter is based on its significant as perceived to overall water quality. Then the index is further determined as the weighted average of all observations of interest (Stambuk-Giljanovic, 1999; Pesce and Wunderlin, 2000; Sargaonkar and Deshpande, 2003; Liou et al., 2004; Tsegaye et al., 2006).

CHAPTER 3: MATERIALS AND METHODS

3.1 Preamble

This chapter described the steps and procedures that were followed in order to accomplish the objectives of this project as well as the methodology and tools that were used for data collection.

3.2 Sampling Methods

3.2.1 Collection and preservation of samples

Water samples were randomly collected from 20 primary schools, 15 private boreholes and 3 communal boreholes within Vhembe district, Limpopo province, South Africa as shown in Table 3.1. In the field, the 500 mL sterile sampling bottles and caps were rinsed three times with water to be sampled before sampling. Samples were collected directly from tap after allowing water to run for at least 5 minutes in order to avoid variations in electrical conductivity (EC) and temperature (Reimann, 2003). Triplicates samples were collected for analytical, heavy metals and microbial analyses. Hence, a total of 114 water samples were collected for each season. Each sample were transferred into a cooler box with ice immediately after collection. Samples were transported to the University of Venda laboratory at -4^{o}C in order to prevent microbial growth and to reduce the rate of chemical reactions in the water samples. Enumeration of total coliform and *Escherichia coli* were carried out within 6 hours of sample collection (SANS 241, 2015).

3.3 Samples Analysis

3.3.1 Analytical measurements

Physicochemical parameters such as pH, and Electrical conductivity (µS/cm) and temperature of groundwater samples were measured in the field by a YSI Professional Plus meter (YSI Inc, Yellow Springs, OH, USA). The YSI Professional Plus meter was calibrated in a buffer solution of pH of 4, 7 and 10 as according to the manufacturer’s instructions. Turbidimeter (Orbeco Hellige, Sarasota, FL, USA) was used to measure the turbidity of the samples. The turbidimeter was calibrated using buffer solutions (1 NTU, 10 NTU, 100 NTU and 1000 NTU) as standards. Measured concentrations were compared with the South African water-quality standards limits, pursuant to the Water Services Act of 1997. Salinity was measured on-site in mg/L using an Extech multimeter.

Each sample was analysed in triplicate to improve validity of the results. From three detected consecutives values, the average values were determined and recorded for further statistical analysis via Microsoft Excel, SPSS and GSS software.

3.3.2 Digestion and analysis of heavy metals

Immediately after collection, samples for heavy metals determination were preserved using HNO_3 on sites and digested the same day of sample collection in the laboratory. Digestion of heavy metals were achieved through Mar6 Microwave Digester which is engineered to run through standard Method of EPA 3015a for aqueous sample. The sample of 45 mL was added into the digestion vessel followed by addition of 5 mL of HNO_3. Before transferred to the microwave digester, the mixture was gently homogenized by swirling the vessel and kept open for 15 minutes to prevent excessive venting, abnormal wear and tear. The microwave ran for 15 mins and the digested samples were allowed to cool for another 15-30 mins. The digested samples were dispatched to the Agricultural Research Council (ARC) for heavy metals analysis using inductively coupled plasma mass spectrophotometer.

3.3.3 Anions using ion chromatography (IC)

For anion concentration, samples were filtered through 0.45 µm syringe filter and placed in an autosampler connected to Metrohm 850 Ion Chromatograph (IC) supplied by Metrohm, Switzerland (Edokpayi *et al.,* 2015). Calibration standards for measured anions; fluoride, chloride, nitrate and sulphate were prepared from two multi-element standards. 1 mg/L, 5 mg/L, 10 mg/L and 20 mg/L were prepared by serial dilution from a stock solution of 100 mg/L. The eluent applied was a combination of Na_2CO_3 and $NaHCO_3$; prepared by weighing accurately 0.168 g and 0.6784 g into 2 L volumetric flask and filled to the mark using ultrapure water, while 0.5M sulfuric acid was used as a regenerant solution. The IC was used for the assay at 0.7 mL/min flow rate with maximum and minimum pressure of 15.0 mPa and 0.1 mPa respectively.

3.3.4 Bacteriological analysis

Groundwater samples collected from the primary school, private household and communal borehole taps were analysed for both *Escherichia coli* (*E. coli*) and total coliform bacteria. The microbial analysis was achieved by a vacuum manifold membrane filtration method, according to method 10,029 provided by Hach Company (2018) following the EPA Protocol of June 30, 1992 . Hot-water bath was set to 100°C and turned on to allow water to boil.

A plastic PVC funnels and cups of manifold were sterilized by boiling at 100℃ in a hot-water bath for 15 mins. Reverse osmosis water was flushed through the apparatus to cool the sample funnels and cups. 0.45 µm filter paper with diameter 47 mm (EMD Millipore, Billerica, MA, USA) was used for filtration (Edokpayi et al., 2021). The filters were aseptically placed on the filtration units using sterilized forceps. A reverse osmosis dilution water was used as a blank sample while conducting microbial analysis. 2 mL (2×10^{-6} m^3) of selective growth media solution (m-ColiBlue24, EMD Millipore, Billerica, MA, USA) was dispersed to an absorbent pad. Filter paper disk with the filtrate was transferred into a petri dish containing absorbent pad and incubated at 35°C (308.15 K) for 18–24 h. Colonies with blue colour were taken to be *E.coli* isolates, mean while other coliforms were red in colour; the total coliforms were the sum of blue and red colonies (Smith, 2001; Hach Company, 2018).

3.3.5 Quantitative human health risk assessment

i) Exposure dose of heavy metals to human

Human exposure risk pathways of an individual to trace metals contamination could be through three main pathways including inhalation via nose and mouth, direct ingestion and dermal absorption through skin exposure. Common exposure pathways to water are dermal absorption and ingestion routes. Exposure dose for calculating human health risk with dermal absorption and ingestion routes have been explained in most conducted projects and can be determined through Equation 3.1 and 3.2 as modified from the USEPA risk assessment guidance for superfund (RAGS) methodology (USEPA, 1989; Li and Zhang, 2010; Asare-Donkor *et al.,*, 2016; Edokpayi et al., 2018b).

$$\mathrm{Exp_{ing}} = \frac{\mathrm{C_{water}} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \tag{3.1}$$

$$\mathrm{Exp_{derm}} = \frac{(\mathrm{C_{water}} \times \mathrm{SA} \times \mathrm{KP} \times \mathrm{ET} \times \mathrm{EF} \times \mathrm{ED} \times \mathrm{CF})}{(\mathrm{BW} \times \mathrm{AT})} \tag{3.2}$$

Where, $\mathrm{Exp_{ing}}$ refer to exposure dose via ingestion of water (mg/kg/day); $\mathrm{Exp_{derm}}$ refers to exposure dose due to dermal absorption (mg/kg/day). Table 3.1 presents exposure dose parameters through ingestion and dermal exposure to water (mg/kg/day) while Table 3.2 shows the dermal permeability coefficient (Kp) in the measured water in cm/h.

Table 3.1: Parameters of exposure dose via ingestion (equation 3.1) as adopted from Edokpayi et al *et al.* (2018b)

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Symbol	**Description**	**Quantity (Adult)**	**Quantity (Children)**
C_{water}	Average concentration of metal in µg/L	As determined for each selected metal	As determined for each selected metal
IR	Ingestion Rate	2.2 L/day	1.8 L/day
EF	Exposure frequency	365 days/year	365 days/year
ED	Exposure duration	70 years	6 years
BW	average body weight	70 kg	15 kg
AT	averaging time in 365 days per year	70 years	6 years
SA	skin area exposure	18,000 cm^2	6600 cm^2
ET	Exposure time	0.58 h/day	1 h/day
CF	Unit Conversion factor	0.001 L/cm^3	0.001 L/cm^3

Table 3.2 The quantity of dermal permeability coefficient (Kp) as adopted from Naveedullah *et al.* (2014)

Selected Element(s)	**Quantity**
Mn, Cu, Cd and Fe	0.001
Cr	0.002
Zn	0.0006
Pb	0.004

ii) Potential non-carcinogenic risks of human exposure to heavy metals

Potential non-carcinogenic risks due to exposure of heavy metals was determined by comparing the calculated contaminant exposures for each exposure route (ingestion and dermal) with the reference dose (R*f*D) for an individual (USEPA, 1989) using Equation 3.3 in order to develop hazard quotient (HQ) toxicity potential of an average daily intake to reference dose for an individual via the two pathways using Equation.3.4.

$$\mathrm{HQ_{ing/derm}} = (\mathrm{Exp_{ing/derm}})/(\mathrm{RfD_{ing/derm}}) \qquad (3.3)$$

Where $\mathrm{RfD_{ing/\,derm}}$ is ingestion/dermal toxicity reference dose (mg/kg/day). The $\mathrm{RfD_{ing}}$ and $\mathrm{RfD_{derm}}$ values applied were adopted from the literature (USEPA, 1989; Wu, *et al.*, 2009; Li and Zhang, 2010; Qbal and Shah, 2013; Asare-Donkor *et al.,* 2016). An HQ value <1 is assumed to be safe (USEPA, 2009), but HQ value exceeding 1 is assumed to be a major potential health concern in association with overexposure of humans to the contaminants.

In order to evaluate the total potential non-carcinogenic effects posed by more than one metal and pathway, the sum of the calculated HQs across metals was stated as hazard index (HI) using Equation 3.4 (USEPA, 1989). The HI greater than 1 indicate the vulnerability of groundwater that could pose adverse potential effect on human health (Li & Zhang, 2010; Naveedullah, Yu, Shen, Duan, & Shen, 2014).

$$HI = \sum_{i=1}^{n} \mathrm{HQ}_{\mathrm{ing/derm}} \tag{3.4}$$

Where, $\mathrm{HI}_{\mathrm{ing/derm}}$ is a hazard index posed by direct ingestion or dermal contact. Chronic daily intake (CDI) of heavy metals via ingestion will be computed through Equation 3.5.

$$CDI = \mathrm{C}_{\mathrm{water}} \times \frac{BW}{DI} \tag{3.5}$$

Where $\mathrm{C}_{\mathrm{water}}$, and represent the concentration of trace metal in the measured water (mg/kg), DI is the average daily intake of water (2.2 L/day for adults and 1.8 L/day for children) and BW is the body weight (70 kg was considered for adult's weigh and 15 kg for body weight of children).

iii) Carcinogenic risk (CR) of human exposure to heavy metals in groundwater

Carcinogenic risk (CR) through ingestion pathway was computed by means of Equation. 3.6:

$$\mathrm{CR}_{\mathrm{ing}} = \frac{\mathrm{Exp}_{\mathrm{ing}}}{\mathrm{SF}_{\mathrm{ing}}} \tag{3.6}$$

Where, $\mathrm{CR}_{\mathrm{ing}}$ denotes carcinogenic risk through ingestion route and $\mathrm{SF}_{\mathrm{ing}}$ denotes carcinogenic slope factor. The SF of Cd is 6.1E+03, Pb is 8.5E+00 and Cr is 5.0E+02 (µg/kg/day) (qbal and Shah, 2013; Naveedullah *et al.,* 2014; Asare-Donkor *et al.*, 2016).

3.3.6 Quantitative Microbial Risk Assessment (QMRA)

Risks of infection and illness of school children and adult due to drinking of groundwater was evaluated using a quantitative microbial risk assessment (QMRA). The QMRA method involves hazard identification, dose-response valuation, exposure assessment, and risk characterisation. Hazard identification involved identification of the pathogens and the nature of adverse health effects (Whelan et al., 2014; WHO, 2016; Odiyo *et al.*, 2020). According to Machdar *et al.*, (2013), only 8% of *E. coli* detected is pathogenic. Therefore, to compute dose assessment for *E. coli*, the detected value was multiplied by a factor of 0.08.

For the purpose of this study, beta-Poisson model (Equation (3.7) has been employed which involves the dose-response calculation which establish the correlation between the dose of pathogens and probability of illness. The dose-response relationships (Table 3.3) were adopted from Shinagawa and Yoshida (1997), Teunis et al., (2004), the U.S. Department of Agriculture/Food Safety and Inspection Service and U.S. Environmental Protection Agency (2013), Machdar *et al*., (2013) which offers a summary of dose-response relationships for a waterborne pathogen (E. *Coli* 0157) based on existing literature.

$$P_{inf}=1-\left(1+\frac{D}{\beta}\right)^{-\alpha} \qquad 3.7$$

Whereby P_{inf} denote for the probability of infection per day, D is signify for the average dose ingested, alpha (α) and beta (β) are the dose-response parameters. The average dose ingested was determined by multiplying the volume of water ingested per day by the recorded average value of the computed pathogen for the three sampling periods. The ingested volume of water of 1 litre per day per child and adult was adopted from Ahmed *et al*. (2020).

Table 3.3 Dose-response assessment parameters adopted from Ahmed *et al*. (2020).

Pathogenic Strain	**Age group**	**Parameters**
E. *Coli* 0157	Child	α =0.084
	Adult	α =0.050
	Child	β =1.44
	Adult	β =1.001
	All age group	Pill/in = 0.35

For the exposure assessment, it was considered that the learners and teachers at school were vulnerable to pathogens through consumption of groundwater for 203 days in the year 2019, meanwhile the community residence who rely on household and communal borehole were considered exposed for 365 days in the year 2019. The risks of annual infection and illness were calculated by means of Equations (3.8) and (3.9), respectively.

$$P_{infannual}=1-(1-P_{inf})^{n} \qquad 3.8$$

$$P_{ill}=P_{infannual}\times P_{ill/in} \qquad 3.9$$

Whereby $P_{infannual}$ denote for the probability of annual infection, n is the number of days of vulnerability in a year, P_{ill} is the probability of illness, and $P_{ill/in}$ the probability of illness per infection. $P_{ill/in}$ values were adopted from Ahmed *et al*., (2020).

The risks of infection per day was computed by values for the months of August, October and November 2019, while the risks of infection per year were determined based on average values for the three-month period.

3.4 Validation of analytical methodology

In order to validate the analytical methodology employed in this study, recovery studies were performed. The known concentrations of the test determinant were added to the samples. The concentrations of both the spiked and real samples were calculated to obtain the percentage recovery (Ata et al., 2015; Edokpayi et al., 2021).

3.5 Statistical Analyses

The IBM SPSS statistics 26, GSS and Microsoft excel 2019 statistical software package were used throughout this study for analysis. The analytical raw data was processed, analysed and graphs plotted using Microsoft Excel. The experimental data obtained were compared with DWAF (1996), SANS 241 (2015) and WHO (2011) guidelines for domestic water use. The physico-chemical concentrations, microbial levels and questionnaire's raw data were kept electronically in excel sheet during the study period. The questionnaire's characteristics were of a categorical nature describing certain water, hygiene and sanitation practices at the household level. The IBM SPSS statistics 26 package were used in the process of cleaning and editing the data and to do comparative analyses. Statistical data were summarized in making use of frequencies, percentages and cross-tabulation.

For the purpose of this study, a Pearson correlation was employed to measure a linear association between two normally distributed random variables data, especially where the change in magnitude of 1 variable is associated with a change in another variable. The correlation could either be a positive correlation (same direction) or a negative correlation in case of the opposite direction. The Pearson correlation coefficient (r) is typically used for jointly normally distributed statistical data (data that follow a bivariate normal distribution) (Mukaka, 2012; Schober et al., 2018). Correlation coefficients are scaled in the range from –1 to +1. It should also be noted that coefficient of Zero (0) suggests that there is no linear relationship. A Pearson correlation coefficient (r) is interpreted based on range; 0.00–0.10 (Negligible correlation), 0.10–0.39 (Weak correlation), 0.40–0.69 (Moderate correlation), 0.70–0.89 (Strong correlation) and 0.90–1.00 for a very strong correlation (Schober et al., 2018).

3.6 Natural Factors controlling water chemistry

3.6.1 Hydrogeochemistry of groundwater

Generally, fundamental factor shaping the ions concentration is the lithology of aquifer (Siwek et al., 2013).The mechanism in controlling water chemistry and possible functional sources of dissolved ions was evaluated by plotting the ratio of equations 3.10. and 3.11 as functions of total dissolved solid (Gibbs, 1970).

$$\text{Cations} = \frac{\text{Na} + \text{K}}{\text{Na} + \text{K} + \text{Ca}} \qquad (3.10$$

$$\text{Anions} = \frac{\text{Cl}}{\text{Cl} + \text{HCO}_3} \qquad (3.11)$$

Equation 3.10 and 3.11 was programmed into microsoft excel (Microsoft 365 MSO version 2102) to generate plots which are integrated in Gibbs diagram as modified from literature review 2.9.4 (Figure 2.2). In this study, Piper diagram were drawn by the Geochemistry's spreadsheet (GSS) software. GSS software produce piper diagram in such that the percentages of milliequivalents of the main cations and anions are plotted in several triangles. The plotted points in the triangular fields were further projected into the central diamond field which gives the overall water character as adapted from literature review in figure 2.1 (Kumar, 2013).

3.7 Water Quality Index (WQI)

3.7.1 Calculation of WQI

For calculating WQI, the index developed by Horton (1965) and modified by Tiwari and Mishra (1985) was used for the purpose of this study. The weighed index method was used to calculate WQI to determine groundwater suitability for drinking purposes. A total of eleven parameters were selected for computing the sum of relative weight (Table 3.3). Each selected parameter apportioned a weight (w_i) based to its relative significance when considering the overall water quality for drinking purposes (Table 3.3). The standards for drinking water as developed by DWAF (1996), WHO (1997), WHO (2008), WHO (2015) and SANS 241 (2015) was used for the computation of WQI. The scale weights were referred from Sener and Davraz, (2013) whereby special weights (*wi*) in a scale of 1 (least significance on water quality) to 5 (uppermost significance on water quality) was allocated to each parameter, based on its implication on human health and its relative enormousness in the quality of drinking water.

The maximum weight of 5 was assigned to the nitrate due to its major importance in water quality assessment. Mg was given the minimum weight of 1 because Mg itself may not be harmful in water at a range within 0 to 70 mg/L (DWAF, 1996).

Any parameter whose occurrence level is above the critical concentration could result in limited usage of the resource for domestic uses and drinking purposes in order to avoid negative impact on human health. Therefore, the aforementioned statement causes the parameter to be assigned for the highest weight of five (Varol and Davraz, 2014). The minimum weight of 1 was assigned to the bicarbonate, total Hardness as $CaCO_3$ and Zn, because its concentration in drinking water is more of aesthetic property than health concerns (SANS 241, 2015; Madhav *et al.,* 2018; Ram et al., 2021).

A weight of 2.0-2.9 was allocated to EC (2.0), Cl (2.8), Mg (2.7), Fe (2), Ni (2) and Cu (2) based on their significant and literature (Khan et al., 2020; Banda and Kumarasamy, 2020; Ram et al., 2021). A weight of 2 was also assigned for Cobalt in this study. Several organisations have no any health-based guidelines proposed for Cobalt, because its naturally found in low concentration (Elumalai, 2017). Moreover Cobalt, was not included in WQI by several studies (Elumalai, 2017; Olasaji et al., 2021; Madilonga et al., 2021). Calcium falls under major cations which is moderately monitored in South Africa. Hence, this parameter was assigned 3 which correlates with other values in the literatures (Banda and Kumarasamy, 2020). A total of three parameters (pH, SO_4^{2-} and Na) were allocated a weight score of 4 as they are adequately monitored for health concern in drinking water.

Based on previous studies covered of the study area, nitrate, fluoride, Lead and Chromium in the groundwater are of major health concern in Vhembe District Municipality (Srinivasamoorthy et al., 2008; Odiyo and Makungo, 2012; Durowoju et al., 2020; Olasaji et al., 2021; Madilonga et al., 2021). Moreover, Nevondo et al. (2019) reported 0.09-2.12 µg/L of Hg concentration in groundwater which evidence the probability of groundwater pollution by mercury from landfill in Thohoyandou, South Africa. The evidence of high concentrations of these parameters in the Vhembe region causes researchers to assign highest value of 5 as they should be monitored closely in the region as implemented in this study. Moreover, the assigned weight score also correlates with the studies conducted in Uttar Pradesh, India and Limpopo region, South Africa by Madhav et al. 2018, Molekoa et al. (2019), respectively just to name a few among others.

The values of weight and relative weight of overall physico-chemical parameters used in this study for computing WQI is displayed in Table 3.4. The relative weight (*Wi*) was determined using equation 3.12:

$$\mathrm{Wi} = \frac{wi}{\sum_{i=1}^{n} wi} \qquad (3.12)$$

Whereby, W_i is the relative weight. Meanwhile, *wi* is the weight allocated for each parameter, and n denotes number of parameters. The quality rating (*qi*) for each parameter was worked out by dividing its actual concentration of each water sample by its assigned standard limits values recommended by the WHO, DWAF and SANS (Table 3.3) and then the answer was multiplied by 100 as displayed on equation 3.13:

$$q_i = \frac{Ci}{Si} \times 100 \qquad (3.13)$$

Where, *qi* denotes quality rating, *Ci* denotes for actual level of each physico-chemical parameter in per groundwater sample in mg/L unless stated, and *Si* represent standard limit set for drinking water quality per measured parameter as specified by WHO, DWAF and SANS (Table 3.4). To calculate for WQI, the product of SI*i* value was determined using equations 3.14 and 3.15.

$$\mathrm{SI}i = \mathrm{Wi} \times \mathrm{qi} \qquad (3.14)$$

$$\mathrm{WQI} = \_\mathrm{SI} \qquad (3.15)$$

Where, SI*i* is the sub-index of the ith parameter; *qi* is the quality ranking which is subject to the amount of *i*th parameter. For easy classification, WQI standards are separated into five classes: Excellent (for less than 50), Good (equal/above 50 but, less than 100), Poor (equal/above 100 but, less than 200), very poor (equal/above 200 but, less than 300) and unsuitable for drinking (greater than 300) (Sahu and Sikdar, 2008; Singh et al., 2016).

Table 3.4: Parameters of concern with assigned weight ratings and weightage coefficients as used in this study based on standard limits.

Parameters	**Weight**	**W_i (Relative Weight)**	**Standard in mg/L (SANS 241:2015)**
pH	4	0.0640	5-9.7
EC (mS/m)	2	0.0320	170
Cl^-	2.8	0.0448	250 (WHO, 2008)
NO_3^-	5 (Madhav et al., 2018)	0.0800	50 (WHO, 2005)
F^-	5 (Madhav et al., 2018)	0.0800	1.5
SO_4^{-2}	4	0.0640	500
HCO_3^-	1 (Madhav et al., 2018)	0.0160	600 (WHO, 1997)
Ca	3	0.0480	32 (DWAF, 1996)
Mg	2.7	0.0432	50 (WHO, 2015)
K	2	0.0320	12 (WHO, 1997)
Na	4	0.0640	200
Mn	5 (Olasoji et al., 2019)	0.0320	0.4
Cr	5 (Olasoji et al., 2019)	0.0800	0.05
Co	2	0.0320	0.5
Ni	2 (Ram et al., 2021)	0.0320	0.07
Cu	2 (Ram et al., 2021)	0.0320	2
Zn	1 (Ram et al., 2021)	0.0160	5
Hg	5	0.0800	0.006
Pb	5 (Madilonga et al., 2021)	0.0800	0.01
Fe	2 (Ram et al., 2021)	0.0320	2
Total Hardness	1 (Ram et al., 2021)	0.0160	500
		Sum of W_i=1.0000	

CHAPTER 4: THE EVALUATION OF MICROBIAL AND PHYSICOCHEMICAL CONTAMINANTS ASSOCIATED WITH GROUNDWATER FROM COLLINS CHABANE AND MAKHADO MUNICIPALITY

4.1 Potential of Hydrogen (pH)

The level of pH ranged between 6.80-8.10, 6.80-10.9 and 6.8-7.9 for the selected schools, household and communal borehole samples, respectively (Table 4.1 to 4.3). The results indicate that aquifer conditions of groundwater samples vary from slightly acidic to alkaline.

The obtained mean values for schools in the month of August, October and November was 7.29±0.21, 7.31±0.41 and 7.43±0.29, respectively while, the computed household values were 7.26±0.36, 7.27±0,23 and 7.66±1.02, respectively. Meanwhile, the mean values of communal borehole were 7.27±0.45 (August), 7.55±0.35 (October) and 7.15±0.15 (November) during the period of investigation.

These pH results were similar with the finding of Odiyo and Makungo (2012) and Durowoju (2015). Although these pH values are above the neutral value of 7.0, they are still within the recommended South African guidelines value of 5.0 to 9.7 for domestic water use (Appendix Table 4.1) apart from pH level of 10.83 which was recorded for household P4 during wet season (November, 2019). Jose et al. (2014) confirmed that majority of soaps used for laundry purposes usually have a pH in the range of 9 to 10. Therefore, the activities such as washing of kitchen dishes, vehicle or laundry with soupy water within the locality of the borehole can affect the pH of groundwater.

High pH levels were obtained during the month of November in comparison to both month of August and October in sample sites S6, S9, S12 and S18 (Table 4.1). The same condition repeated for household sites P1, P4, P8, P13-14 (Table 4.2). A huge spike of pH levels in the month of November could be due to contamination of groundwater by infiltration during rain events.

Table 4.1: Average values for physico-chemical parameters in groundwater sample collected from Schools in Makhado and Collins Chabane Municipality throughout the study.

Sample Code	Salinity (mg/L)			pH			EC (µS/cm)			TDS (mg/L)			Turbidity (NTU)		
	August	October	November	August	October	November	August	October	November	August	October	November	August	October	November
S1	485	430	387	7.4	8	7.8	924	941.3	1020.3	600.6	611.8	663.2	0	0	0
S2	661	593	492	7.8	7.7	7.7	1202	680	1125.3	781.3	442	731.5	0	0	0
S3	202	348	385	7.4	**	7.4	449.9	**	756.7	292.4	**	491.8	0	**	0
S4	296	325	326	7.5	7.4	7.4	617	544.5	683	401.1	353.9	444	0	0	0
S5	278	**	301	7.2	**	7.3	581	**	618.7	377.7	**	402.1	0	**	0
S6	597	405	338	7.1	7	7.6	781	872	723.3	507.7	566.8	470.2	0	0	0
S7	188	176	191	7.2	7.2	7.2	417.7	242.5	446.1	271.5	157.6	290	0	0	0
S8	371	247	246	7.1	7.1	7.2	472.2	562.5	491.5	306.9	365.6	319.5	0	0	0
S9	328	307	228	7.4	7.4	7.7	617	710	653	401.1	461.5	424.5	0	0	0
S10	120	148	116	7.2	7.2	7.1	351.4	424.8	393.6	228.4	276.1	255.8	0	0	0
S11	187	225	165	6.9	6.9	7.1	420.7	506.3	418.3	273.5	329.1	271.9	0	0	0
S12	298	257	193	7.3	7.3	7.6	388.7	448.1	430.5	252.7	291.3	279.8	0	0	0
S13	216	210	209	7	7.4	7.1	398.7	448.3	466.3	259.2	291.4	303.1	0	0	0
S14	507	355	310	7.2	7.2	7.5	679	591.9	806.7	441.4	384.8	524.3	0	0	0
S15	349	235	178	7.6	7.3	7.7	448	470.3	472.6	291.2	305.7	307.2	0	0	0
S16	209	278	175	7.4	7	7.6	519	547.7	575.7	337.4	356	374.2	0.4	0	0
S17	185	302	248	7.4	7.3	7.5	432.9	626.3	667.7	281.4	407.1	434	0	0	0
S18	254	277	281	7.1	8.1	8	566	581.3	617.7	367.9	377.8	401.5	0.3	0	0
S19	330	286	337	7.3	7.2	7.2	688	713.5	704.3	447.2	463.8	457.8	0	0	0
S20	**	315	293	**	6.8	6.8	**	838	631.7	**	544.7	410.6	**	0	0
S21	**	200	**	**	8.4	**	**	484.6	**	**	315	299.4	**	0	**
Min	120	148	116	6.9	6.8	6.8	351.4	242.5	393.6	228.4	157.6	255.8	0	0	0
Max	661	593	492	7.8	8.4	8	1202	941.3	1125.3	781.3	611.8	731.5	0.4	0	0
mean	319.00	295.95	269.95	7.29	7.36	7.43	576.54	591.26	635.15	374.77	384.32	407.45	0.04	0.00	0.00
STD	144.44	97.97	90.17	0.21	0.41	0.29	207.06	166.84	188.64	134.59	108.44	122.08	0.11	0.00	0.00

** = Sample not measured due unavailability of borehole water

Table 4.2: Average values for physico-chemical parameters in groundwater sample collected from individual household in Makhado and Collins Chabane Municipality throughout the study.

Sample Code	Salinity (mg/L)			pH			EC (µS/cm)			TDS (mg/L)			Turbidity (NTU)		
	August	October	November	August	October	August	October	November	August	October	August	October	November	August	October
P1	310.6	348.1	340	7.1	7.2	7.5	647	725.3	460.7	420.6	471.4	744.9	0	0	0
P2	126.8	**	514	8.3	**	7.2	264.1	**	1146	171.7	0	744.9	0	0	0
P3	331.2	360.5	234	7.2	7.1	7.3	690	751	812	448.5	488.2	527.8	0.4	0	0
P4	175.5	172.7	181	6.9	7.1	**10.9**	365.7	359.8	385.5	237.7	233.9	250.6	0	0	0
P5	259.2	307.5	278	7.2	7.2	7.3	540	640.7	**	351	416.4	0	0	0	0
P6	265.4	283.3	255	7.3	7.1	7	553	590.3	495.2	359.5	383.7	321.9	0	0	0
P7	478.6	514.7	488	7.1	7.1	6.9	997	1072.3	916	648.1	697	595.4	0	0	0
P8	465.6	499.3	490	7.1	7.2	7.6	970	1040.3	766.3	630.5	676.2	498.1	0	0	0
P9	299	163.3	307	7.3	7.5	7.3	623	340.3	781.3	405	221.2	507.9	0.1	0	0
P10	348.5	393.6	383	6.9	7.3	7.3	726	820	619.7	471.9	533	402.8	0	0	0
P11	487.2	**	**	7.6	**	**	1015	**	**	659.8	**	**	0	0	0
P12	1932	2111	288	6.8	7	**	4025	4398	**	2616.3	2858.7	0	0	0	0
P13	345.1	391.5	371	7.2	7.5	8	719	815.7	764	467.4	530.2	496.6	0	0	0
P14	408	464	378	7.2	7.3	7.6	850	966.7	778.5	552.5	628.3	506	0	0	0
P15	447.8	535.7	**	7.7	7.9	**	933	1116	**	606.5	725.4	**	0	0	0
Min	126.8	163.3	181	6.8	7	6.9	264.1	340.3	385.5	171.7	0	0	0	0	0
Max	1932	2111	514	8.3	7.9	10.9	4025	4398	1146	2616.3	2858.7	744.9	0.4	0	0
mean	445.37	503.48	346.69	7.26	7.27	7.66	927.85	1048.95	720.47	603.13	633.11	430.53	0.03	0.00	0.00
STD	410.54	477.82	99.90	0.36	0.23	1.02	855.29	995.47	208.75	555.95	647.77	227.12	0.10	0.00	0.00

** = Sample not measured due unavailability of borehole water

4.1.1 Electrical Conductivity

There was a significant correlation ($p < 0.01$) between TDS, EC and salinity (Table 4.6). The EC and TDS values for all collected samples within selected primary schools, individual household and communal boreholes were within the SANS (2015) recommended limits of <1700 µS/cm and <1200 mg/L except for P12 sample (439.8 mS/m and 2858.7 mg/L) collected from individual household in October 2019 (Table 4.2). Therefore, these two parameters pose no threat to human health among groundwater collected in schools.

The recorded EC values for school samples during August, October and November, 2019 ranged from 351.40 - 1202.00, 242.50 - 941.30 and 393.60 - 1125.30 µS/cm, with the mean values of 576.54±207.06, 597.18±166.84 and 635.15±188.64 µS/cm, respectively.

The results suggest that groundwater collected from sample S2 was slightly salty (>1000 µS/cm) except for the period of October, 2019. The highest value was obtained in school sample S2 (1202 µS/cm) in the month of August, while in October, lowest concentration was recorded for S7 borehole (242 µS/cm) (Table 4.1).

Table 4.3: Average values for physico-chemical parameters in groundwater sample collected from communal boreholes in Makhado and Collins Chabane Municipality throughout the study.

	Salinity (mg/L)			pH			EC (µS/cm)			TDS (mg/L)			Turbidity (NTU)		
Sample Code	**August**	**October**	**November**	**August**	**October**	**August**	**October**	**November**	**August**	**October**	**August**	**October**	**November**	**August**	**October**
C1	230	233.8	**	7.9	7.9	**	479.1	487	**	311.4	316.6	**	0	0	0
C2	301.4	325	294	6.9	7.2	7	628	677	720.5	408.2	440.1	468.3	0.3	0.1	0
C3	279.4	0	303	7	**	7.3	582	**	517.3	378.3	0	336.2	0.9	0	0
Min	230	0	294	6.9	7.2	7	479.1	487	517.3	311.4	0	336.2	0	0	0
Max	301.4	325	303	7.9	7.9	7.3	628	677	720.5	408.2	440.1	468.3	0.9	0.1	0
Mean	270.27	186.27	298.50	7.27	7.55	7.15	563.03	582.00	618.90	365.97	252.23	402.25	0.40	0.03	0.00
STD	29.86	136.87	4.50	0.45	0.35	0.15	62.25	95.00	101.60	40.47	185.35	66.05	0.37	0.05	0.00

** = Sample not measured due unavailability of borehole water

The recorded EC values from sampled households during August, October and November ranged from 264.10-4025.00, 340.30-4398.00, 385.50-1146.00 µS/cm respectively with the mean values of 927.85±855.29, 1048.95±995.47, 720.47 ±208.75 µS/cm.

The results reveals that water samples taken from P12 household boreholes were salty, especially in dry season. For communal boreholes, the range for the month of August, October and November was 479.10-628.00, 487.00-677.00, 517.30-720.50 µS/cm, respectively with mean concentrations of 563.035±62.25, 582.005±95.00, 618.905±101.60 µS/cm, respectively. The highest value was obtained in household P12 (4398 µS/cm) in the month of October, while the lowest was recorded for P2 (264.10 µS/cm) in the month of August (Table 4.2). Based on the EC values, most of the groundwater samples (77.19%) sourced from the communal boreholes is fresh in nature (< 1000 µS/cm) meanwhile private borehole P12 water with EC > 1500 µS/cm could have adverse effects on many crops if used for agricultural practices (Zaman *et al*., 2018; Saha *et al.,* 2019).

4.1.2 Turbidity

The concentration of turbidity suggests the possible contamination due to the presence of pathogens (Edokpayi *et al*., 2018b). The levels of turbidity ranged between 0.0 - 0.40, 0.0 - 0.4 and 0.0 - 0.9 NTU for selected schools, household and communal borehole samples, respectively (Appendix Table 4.2 and 4.3). The average turbidity values of water samples during August, October, November, ranged from 0.0 – 0.86, 0.0 - 0.06, and 0-0.01 NTU, respectively. Considering the turbidity concentration within the standard limits of 1 NTU by WHO (2017) and SANS (2015), the investigated water from boreholes are consider fit for domestic purposes.

4.1.3 Water salinity

For the samples collected from selected schools, the recorded water salinity ranged from 120.00 - 661.00 mg/L (August), 148.00 - 593.00 mg/L (October) and 116.00-492.00 mg/L (November) with the mean concentration value of 319.00±144.44, 301.50±95.67 and 269.95±90.17 mg/L, respectively. For households, the recorded water salinity ranged from 126.80-1932.00 (August), 163.30-2111.00 (October) and 181.00-514.00 mg/L (November) respectively with the mean concentration value of 445.37±410.54, 503.48±477.82, 346.69 ±99.90 mg/L, respectively. Meanwhile, the recorded water salinity concentrations collected from selected communal boreholes during August, October and November, 2019 ranged from 230.00 - 301.40, 233.80-325.00, 294.00-303.00 mg/L, respectively with the mean concentration value of 270.27±29.86, 279.40±136.87, 298.50±4.50mg/L, respectively. The highest values were observed from sample P12 during the month of August and October with an average concentration of 1932 and 2111 mg/L (Table 4.2). There is no health based standard guideline value for salinity (Appendix Table 4.1), however, there is an aesthetic guideline limit value of 200 mg/L recommended by WHO (2017). Several studies have revealed that drinking water with excessive salinity could lead to hypertension including preeclampsia and gestational hypertension (Khan *et al*., 2014; Talukder *et al*., 2017; Al Nahian *et al*., 2018).

4.2 Anions Concentration in Water Samples

The anions concentration in water samples collected for this study has been analysed for dry (August) and wet season (November).

4.2.1 Nitrate

The recorded nitrate concentration for the school samples ranged from 7.02 to 111.14 mg/L and 6.92 to 120 mg/L, all individual household (2.03 to 1532 mg/L and 36.03 to 925 mg/L) and communal borehole (22.27 to 74.76 mg/L and 36.7 to 79.4 mg/L) samples collected from Collins Chabane and Makhado municipality exceeded the WHO permissible limit of <50 mg/L for drinking purposes, respectively throughout the season (Table 4.5). In terms of borehole sites, elevated concentration (> 50 mg/L) has been observed from school (35.00 %, n=19), household (50.00 %, n=14) and communal borehole site (50.00 % , n=2) borehole sites throughout the assessment. Meanwhile in terms of samples, high values (> 50 mg/L) were obtained in school (41.03 %, n=39), household (68.97 %, n=29) and communal samples (40.00 %, n=5).

Low values were also obtained from school samples S4 (12.09-13.03 mg/L), S7 (14.74-15.07 mg/L), S11 (6.92 -7.02 mg/L, S12 (9.51-9.57 mg/L) and household sample P4 (0.06-17.52 mg/L) as shown in Table 4.5. Yu et al. (2020) reported nitrate concentration in the groundwater ranging from 0.075 to 166.4 mg /L. Similar results of mean concentrations of 95.62 ± 80.1 and 98.28 ± 80.57 for NO_3^- were observed from groundwater samples collected in rural areas of Yantai, China during dry and wet season (Yu et al., 2020). Similar study by Ntshangase (2019) has also reported elevated concentration of NO_3^- level (61.6- 179.96 mg/L) during the assessment in Chaneng Village (Rustenburg), South Africa. These similar recorded results were beyond the permissible limit of 50 mg/L as per WHO and SANS 241 limits.

This study has observed that the assessed boreholes such as S6 (111.14-91.51), S14 (103-120 mg/L), P6 (66.29-1532 mg/L) and P12 (846-925 mg/L) were within unsewered areas, most people who inhabit these rural areas prefer septic systems to dispose household (including government facilities) wastewater. Most systems are design in such that they discharge waste into a tank and then release much of the effluent into an underground disposal field. At this stage, the nitrogen which has remains in an organic forms and ammonium find access to reach the aerobic zone which later oxidized to form nitrate (Zhou, 2015). This concentration of nitrate is transported with water into the groundwater during irrigation and heavy rain event during both dry and wet season. Household borehole are located not far away from concentrated livestock with absence of slurry storage facilities and manure tanks (Zhou, 2015).

Table 4.5: Statistical description for Nitrate (NO_3^-) in groundwater sample collected from in Makhado and Collins Chabane Municipality throughout the study.

School boreholes	**NO_3^- (Nitrate) Dry**	**NO_3^- (Nitrate) Wet**	**Household Borehole**	**NO_3^- (Nitrate) Dry**	**NO_3^- (Nitrate) Wet**	**Communal Borehole**	**NO_3^- (Nitrate) Dry**	**NO_3^- (Nitrate) Wet**
S1	**69.78**	**66.7**	**P1**	40.71	36.03	**C1**	22.27	**
S2	**60.31**	**53.34**	**P2**	2.03	**195**	**C2**	**74.76**	**79.4**
S3	**56.26**	38.93	**P3**	**133**	**125**	**C3**	26.95	36.7
S4	12.09	13.03	**P4**	17.52	< 0.06			
S5	**62.89**	**67.95**	**P5**	29.73	**80.66**			
S6	**111.14**	**91.51**	**P6**	**1532**	**66.29**			
S7	15.07	14.74	**P7**	**192**	**206**			
S8	27.69	33.99	**P8**	**204**	**228**			
S9	34.26	35.09	**P9**	45.06	**64.85**			
S10	13.51	13.35	**P10**	**78.76**	**83.92**			
S11	*7.02*	6.92	**P11**	**158**	**119**			
S12	9.57	9.51	**P12**	**846**	**925**			
S13	39.16	48.75	**P13**	42.24	44.44			
S14	**103**	**120**	**P14**	**92.87**	**103**			
S15	28.83	41.08	**P15**	**132**	**			
S16	29.84	27.82						
S17	46.87	**50.13**						
S18	**	48.2						
S19	**88.93**	**89.63**						
S20	**91.48**	**83.64**						
Min	7.02	6.92	Min	2.03	36.03	Min	22.27	36.7
Max	111.14	120	Max	1532	925	Max	74.76	79.4
mean	47.77	47.72	mean	236.39	175.17	mean	41.33	58.05
STD	32.11	30.38	STD	±98.71	224.46	STD	23.72	21.35
Bolded Values = Values exceeded WHO (2004) and SANS 241 (2015) guideline, ** = Sample not measured due unavailability of borehole water								

Long-term exposure to elevated nitrate is associated with gastric problems due to the formations of nitrosamines which have been proven to cause cancer in test animals (Self and Waskom, 2013). Report has discovered that certain birth defects by pregnant woman could be associated with high intake of nitrate from drinking water (Bundy et al., 1980). The high obtained concentration values of nitrate (Table 4.5) in these samples implies drinking water from these boreholes could lead to methaemoglobinaemia, especially to infants (DWAF, 1996).

4.2.2 Phosphate

Values for phosphate (PO_4) in school boreholes samples (0.07 to 1.68 mg/L and below detection limit (bdl)-1.01 mg/L), all individual household (0.04-13.89 mg/L and 0.12-1.24 mg/L) and communal borehole (0.06-0.19 mg/L and 0.1-0.1 mg/L) were obtained in low concentration in groundwater samples collected from Collins Chabane and Makhado municipality in dry and wet season, respectively (Appendix Table 4.2 and 4.3). This study has observed low concentration of phosphate in groundwater. Ntshangase (2019) and Odiyo et al. (2020) recorded the concentration ranges of 0.03 to 0.39 mg/L and 2.05 to 11.59 mg/L, respectively throughout the assessment period. SANS 241 (2015) and WHO (2004) have not set permissible limit for phosphate concentration in drinking water.

4.2.3 Sulphate and Chloride

The recorded sulphate concentration for schools samples ranged between 2.02 to 32.91 mg/L and 2 to 29.7 mg/L, all individual household (2.68- 46.3 mg/L and 5.77-48.98 mg/L) and communal borehole (4.38-15.14 mg/L and 11.69-67 mg/L) during dry and wet season, respectively. The recorded mean values for S1-S20, P1-P15 and C1-C3 were estimated to be 10.28±6.86, 19.65±15.50 and 10.02±4.41 in dry season and 9.97±6.45, 22.37±15.19 and 13.68±1.99 in wet season, respectively (Appendix Table 4.2 and 4.3).

These are below the permissible limits of 400 mg/L and 500 mg/L given by the WHO and SANS 241, respectively (Appendix Table 4.2). Hence, there is no borehole water sample which was found with human health concern with regard to excess concentration of SO_4^{2-}. The recorded chloride concentration during the dry and wet seasons for schools boreholes ranged between 14.12 to 68.58 mg/L and 14.70 to 68.96 mg/L, all individual household (19.16-647 mg/L and 15.13-690 mg/L) and communal borehole (29.43-52.19 mg/L and 53.9-54.85 mg/L) samples were below the SANS 241 (2015) guideline value of <300 mg/L throughout the season except for sample P12. The analytical results from P12 show extremely high concentration values of 646.64 and 690.00 mg/L in dry and wet season, respectively.

WHO (2015) has no set standard limit for chloride in view of its insignificant concentration values reported in drinking water. However, the chloride level which exceeds 250 mg/L is not recommended in drinking water as it could cause perceptible taste (WHO, 2017). Barbieri *et al*. (2019) reported excess content of chloride (229.11- 4262.49 mg/L) found naturally in groundwater samples collected in Kruger National Park, Gaza Province, in the Southern part of Mozambique. However, an increase in chloride concentrations is thought to be due to anthropogenic such as sewage contamination from septic tanks and water softeners used in most household (Jose et al., 2014).

4.2.4 Fluoride

The concentration of fluoride in the primary school water samples ranged from 0.06 to 2.16 mg/L and 0.03 to 2.03 mg/L with the mean fluoride concentration of 0.55 ±0.55 mg/L and 0.54±0.58 mg/L in dry and wet season, respectively (Table 4.6) . All water samples collected from schools complied with 1.5 mg/L of F^- concentration set by SANS 241 (2015) water quality guideline except for water sample taken from S1 site with detected values of 2.16 mg/L and 2.03 mg/L in dry and wet season, respectively (Table 4.6). Since there is no evidence of anthropogenic sources of fluoride contamination, the geologic rocks in the area is the possible source of F^- contamination in S1 borehole (Wu *et al*., 2016). Several studies have shown that groundwater is associated with high concentrations of fluoride due to weathering and leaching of fluoride-bearing minerals from rocks and sediments (Makungo, 2008; Olivier *et al*., 2011; Odiyo and Makungo, 2012; Durowoju *et al*., 2015; Shabalala *et al*., 2015; Onipe et al., 2020).

A concentration of 0.5-1.5 mg/L of F^- is good to human health while ingestion of water via drinking with excessive F^- greater than 1.5 mg/L could pose human health problem such as skeletal and dental fluorosis (Wu *et al.,* 2012; Li *et al*., 2014; WHO, 2017). Therefore, consumption of water from S1 borehole may pose or cause advance health effect on human (Dental fluorosis) using the water for domestic activities and drinking purposes. The average concentration of fluoride in the private household water samples ranged from 0.60±0.33 and 0.64±0.39 mg/L in dry and wet season, respectively. The average concentration of fluoride in the communal water samples ranged from 0.31±0.20 mg/L and 0.30±0.27 mg/L in dry and wet season, respectively. All water samples collected from household and communal boreholes did not exceed the acceptable limits of 1.5 mg/L set by SANS 241 (2015).

Table 4.6: Fluoride concentrations in groundwater collected from Collins Chabane and Makhado municipality during dry and wet seasons

Sample Number	F^- (Fluoride) dry	F^- (Fluoride) wet	Sample Number	F^- (Fluoride) dry	F^- (Fluoride) wet
S1	2.16	2.03	P1	0.03	0.03
S2	1.24	1.27	P2	0.24	0.38
S3	0.89	0.87	P3	0.39	0.37
S4	0.69	0.65	P4	0.14	0.03
S5	0.54	0.52	P5	0.30	0.30
S6	0.29	0.4	P6	0.03	0.20
S7	0.20	0.22	P7	0.46	0.47
S8	0.09	0.03	P8	0.35	0.34
S9	0.33	0.03	P9	0.55	0.54
S10	0.40	0.26	P10	0.45	0.49
S11	0.25	0.15	P11	0.87	**
S12	0.03	0.03	P12	1.24	1.32
S13	0.06	0.03	P13	0.90	0.87
S14	0.24	0.03	P14	0.91	0.91
S15	0.03	0.06	P15	0.96	1.46
S16	0.03	0.03	C1	0.07	**
S17	0.03	0.03	C2	0.28	0.03
S18	**	0.03	C3	0.57	0.57
S19	0.28	0.03			
S20	0.03	0.03			

** = Sample not measured due unavailability of borehole water

Major Cations in the investigated boreholes

4.2.5 Magnesium in sampled water

The mean concentrations of magnesium (Mg) in water samples taken from primary school were 44.25±13.86 mg/L and 42.14± 13.14 mg/L in dry and wet season, respectively (Figure 4.1). About 27.5% of school borehole water samples exceeded the acceptable limits of Mg concentration of 50 mg/L set by WHO (2015) (Figure 4.2). A total of four (4), namely, S1 (58.90-62.00 mg/L), S2 (78.90-79.30 mg/L), S3 (50.60-57.00 mg/L), S19 (53.20-56.40 mg/L) boreholes did not comply in terms of Mg concentration throughout the study period (Figure. 4.1) .

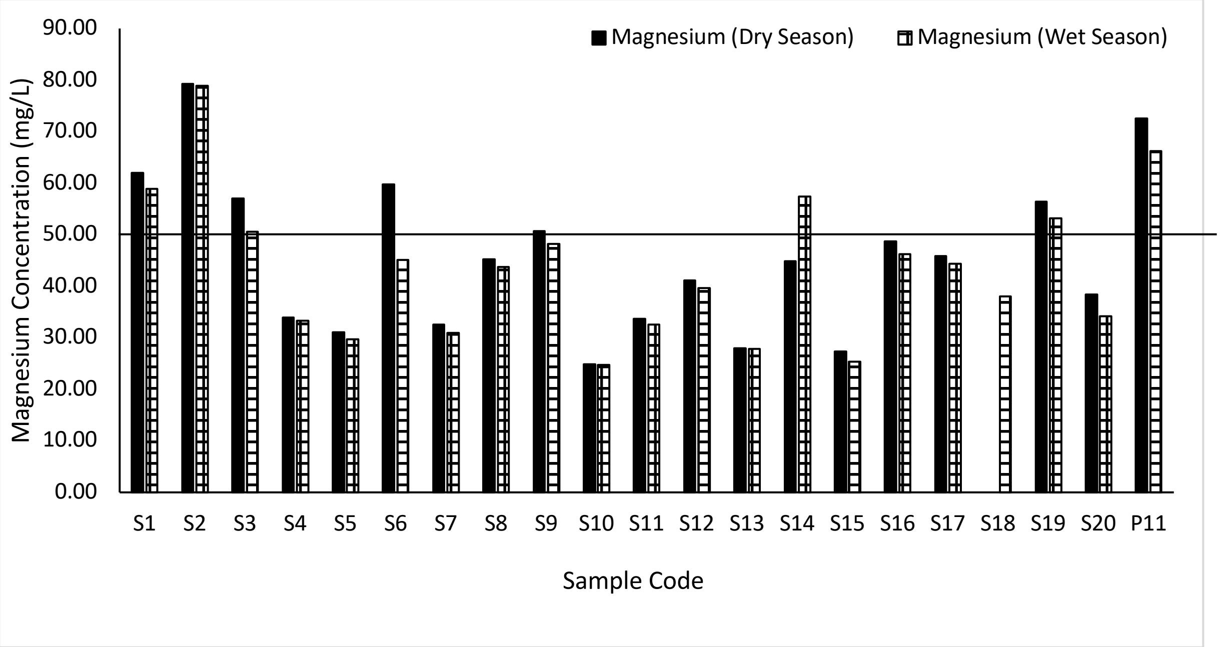


Figure 4.1: Magnesium concentrations in the public primary school boreholes during dry and wet season

In the household water samples, average Mg concentrations were 65.49±67.24 mg/L and 64.46±60.86 mg/L in dry and wet season, respectively (Figure 4.2). The maximum value of concentration detected was 309.00 mg/L and 278.00 from P12 water sample in dry and wet season, respectively. 48.27% of household borehole water samples (n=29) exceeded the tolerable concentration of 50 mg/L as according to WHO (2015) water quality standard guideline (Figure 4.2).

High Mg concentrations could be from run-off effluents and leaching from agricultural activities (DWAF, 1996). Different pattern was observed in all the investigated communal water samples (Figure 4.2). The concentration of all communal borehole samples complied with the WHO (2015) standard limits apart from C2 borehole samples that has Mg level of 52.00 mg/L in dry season (Figure 42). The communal borehole samples recorded a mean Mg levels of 41.23±8.54 and 41.55±8.35 in dry and wet season, respectively.

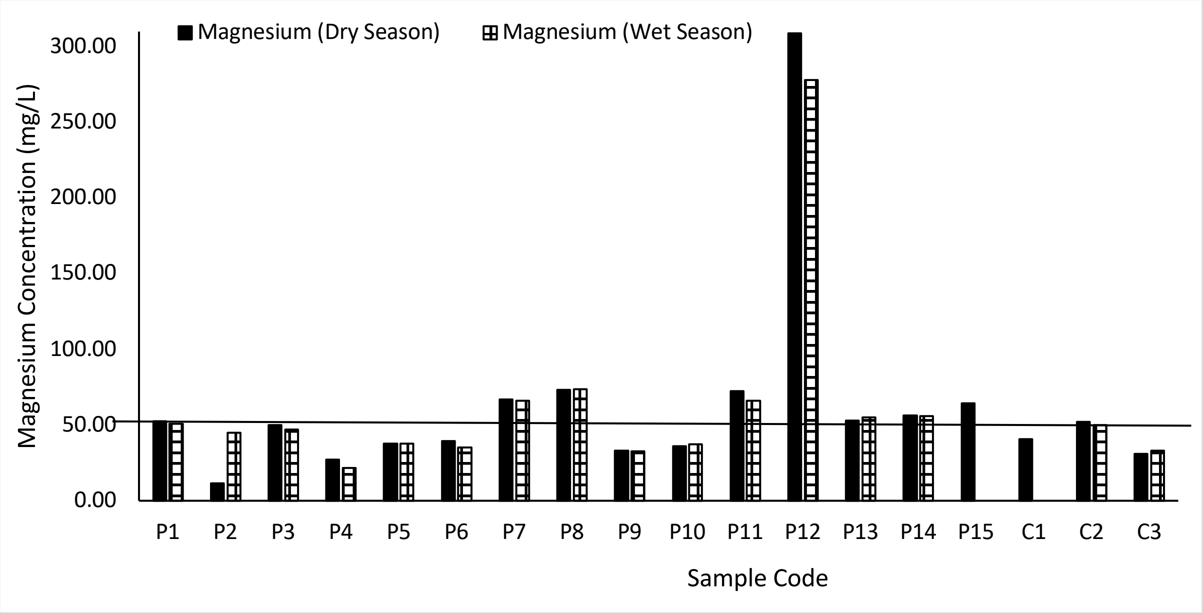


Figure 4.2: Magnesium concentrations for private borehole water in dry and wet season

4.2.6 Calcium ion in the borehole samples

The mean concentrations of calcium in school samples were 35.12±15.08 and 31.39±11.85 mg/L in dry and wet season respectively. All samples collected from school borehole complied with the WHO (2011) standard limit.

A mean concentration of 67.06±77.36 and 62.30±69.64 mg/L were reported in the household borehole samples in the dry and wet season, respectively. British Colombia. (2007a) categorised calcium concentration in water as low (less than 60 mg/L), medium (60-119 mg/L), high (120-179 mg/L), and very high (greater than 180 mg/L). High levels of calcium were obtained in sample P12 at a range between 308 to 349 mg/L.

Nwankwo et al. (2020) conducted a similar study in Bangladesh, which discovered calcium concentration of at range between 11.9 to 366 mg/L with average concentration of 103 mg/l. In this study, medium level of calcium were obtained in P11 (79.2 and 62.9 mg/L), P14 (69.60 and 65.00 mg/L) and P15 (70.3 in dry season) sample in dry and wet season, respectively.

Furthermore, the obtained mean levels of calcium in communal samples were 29.17±8.30 and 28.70±4.50 mg/L in dry and wet season, respectively. All samples collected complied with the standard limits for drinking water throughout the study period which implies that water from is fit for domestic use (DWAF, 1996; WHO, 2011). Nag (2009) reported that the normal concentration of calcium in groundwater range between 10 to 100 mg/L. This concentration are influence by carbonate rocks (dolomites and limestone) which are dissolved by carbonic acid in groundwater (Saha et al., 2019). Ganyaglo et al. (2010) suggested chemical breakdown of pyroxenes and calcic-plagioclase feldspars being a cause of calcium concentration in groundwater. Similar study suggest lime from agricultural fertilisers as a cause to high level of calcium in groundwater (Saha et al., 2019).

Generally, the aforementioned samples with concentration greater than 32 mg/L reveals that groundwater may cause scaling if used on water boilers (DWAF, 1996; WHO, 2011). This study reveals that calcium concentration decrease in wet season as compared to dry season, see Figure 4.3 and 4.4 below. A diminution in calcium levels during rainy season could be as a result of dilution due to recharge in groundwater source.

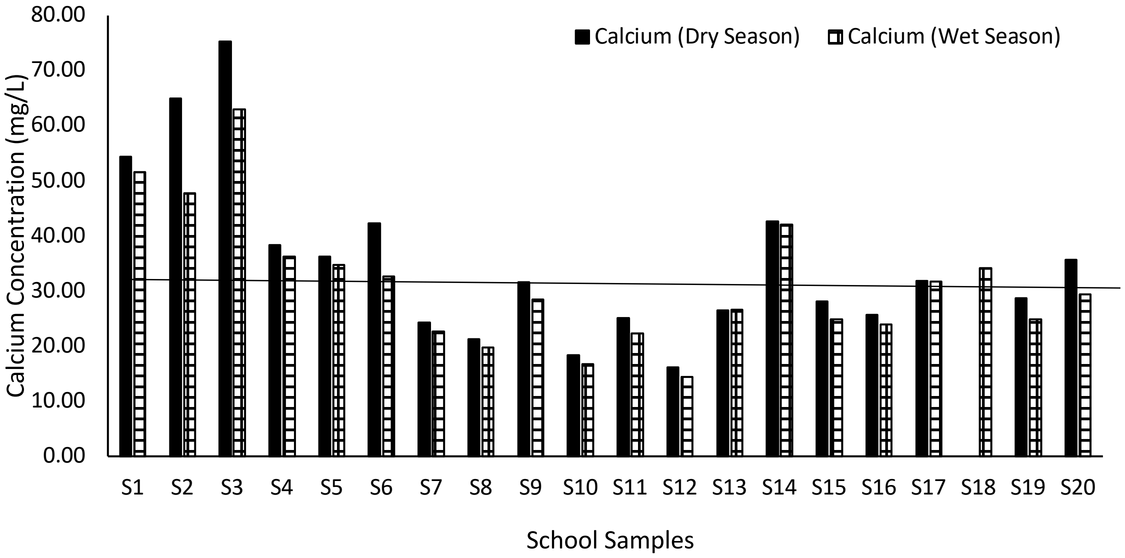


Figure 4.3: Calcium concentrations for public primary school borehole water in dry and wet season

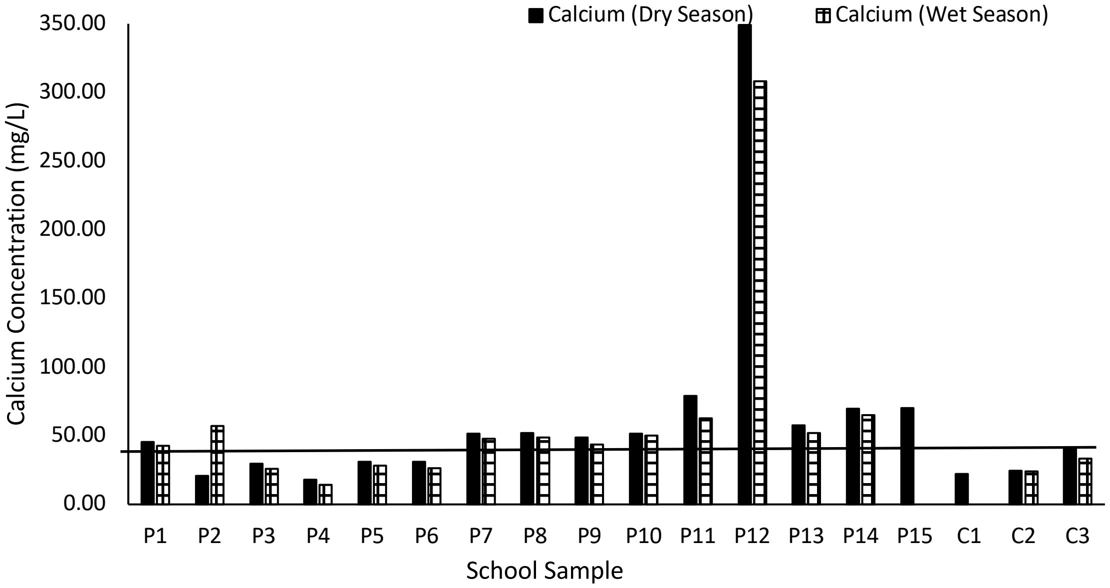


Figure 4.4: Calcium concentrations for individual household and communal borehole water in dry and wet season

4.2.7 Hardness

According to Guidelines for Canadian Drinking Water Quality, water with total hardness of less than 60 mg/L, 60 mg/L to < 120 mg/L, 120 to < 180 mg/L and ≥ 180 mg/L is considered soft, Medium hard, hard and very hard, respectively (British Colombia, 2007b, WHO, 2011). Groundwater samples collected from school (76.92%), household (89.66%) and all communal borehole falls under a very hard category. The recorded range for total hardness as $CaCO_3$ concentration of schools samples (148.48 to 488.61 mg/L and 143.41 to 444.02 mg/L), household samples (99.38 to 2143.92 mg/L and 124.82 to 1913.88 mg/L) and communal borehole (222.12 to 275.81mg/L and 219.62 to 265.92 mg/L) fell beyond soft water category as stated by WHO (2011) during dry and wet season respectively (Table 4.7). The mean values for S1-S20 (437.15±468.44 and 421.03±422.79), P1-P15 (269.93±87.02 and 251.90±75.30) and C1-C3 (242.63±23.68 and 242.77±23.15) fell below 500 mg/L during dry and wet season respectively apart from P12 samples throughout the assessment. The results of this study is comparable with those reported by Khan et al. (2021) in District Bajaur, (Pakistan).

Groundwater associated with a hardness level beyond 200 mg/L could cause scale deposition in pipes and tanks within buildings. Its further result in scum formation and high soap consumption. On heating elements or containers, hard waters could form deposits of calcium carbonate scale. Sample P4, S7, S10, S13 and S15 had TH level between 124.82 to 194.92 throughout the study period which suggest that the aforementioned effects could be minimum (Table 4.4).

There is no health-based guideline value for concentration of hardness in drinking-water. However, in some cases, consumers tolerate water hardness in excess of 500 mg/l which is very hard (WHO, 2011). High concentration of TH was recorded in sample P12 (2143.92 and 1913.88 mg/L) during the dry and wet season, respectively. The use of such high level of TH cause unpleasant taste, stain clothes, deposit on heat boilers and shower taps (Edokpayi et al., 2018a).

4.2.8 Level of Sodium (Na), Potassium (K) and Boron (B) in water samples

The mean concentration of Na in the school borehole is 32.11±14.33 mg/L and 32.71±13.73 mg/L in dry and wet season, respectively. In the private household water samples, the mean levels were 32.58±13.45mg/L and 46.41±23.72mg/L in dry and wet season, respectively which is within the desired limits (Table 4.1). In the communal water samples, the average levels were 25.83±5.60 mg/L and 30.70±2.80 mg/L in dry and wet season, respectively which is within the desired limits (Appendix Tables 4.2 and 4.3).

The mean concentrations of K in the school water were 3.93±2.04 mg/L and 4.02±2.35 mg/L, respectively. While that of the private household were 5.01±3.09 mg/L and 4.97±3.28 mg/L in dry and wet season, respectively. The mean K concentration in the communal were 4.25±2.18 and 4.50±2.69 mg/L in dry and wet season, respectively. They all complied with the desired limits (Appendix Table 4.1). Similar study by Molekoa et al. (2020) in Mokopane, Republic of South Africa has found K concentration at a range between 1.46 to 9.72 mg/L with mean value of 3.45±2.35 mg/L which is within the WHO (2011) permissible limit of 200 mg/L.

Boron is highly soluble in groundwater. Boron based products such as detergents contain high concentration of Boron (B) of which afterward accumulate in septic systems which may leak contaminants to groundwater source (Tamborski et al., 2020). In this study, boron was observed in school sample S1-S20 with concentration between 0.01 to 0.05 mg/L with mean value 0.02±0.01 mg/L which is below the SANS 241 (2015) guideline value (2.4 mg/L) throughout the season. Similarly, sample P1-P15 and C1-C2 showed low concentration which ranges from 0.01 to 0.26 and 0.01-0.2 mg/L with mean concentration of 0.04±0.06 and 0.03±0.05 during dry and wet season. Communal sample C1-C2 scored low concentration which ranges from 0.01 to 0.01 mg/L with mean concentration of 0.01±0.00 mg/L throughout the study period. Similarly, Tamborski et al. (2020) obtained boron concentration between the range of 0.017-0.067 mg/L in Long Island Sound (LIS), NY, United States which is below the SANS 241 permissible limit of 2.4 mg/L. In general groundwater of Makhado and Collins Chabane municipality has no adverse health implication posed by these elements (Na, K and B).

Table 4.7 Statistical description of total hardness concentration in groundwater samples from Collins Chabane and Makhado Municipality in the dry and wet seasons

	Household			**School samples**			**Communal samples**	
S/N	**Dry**	**Wet**	**S/N**	**Dry**	**Wet**	**S/N**	**Dry**	**Wet**
P1	329.40	316.64	**S1**	391.15	371.40	**C1**	222.1248	**
P2	*99.38*	328.30	**S2**	488.61	444.02	**C2**	275.8119	265.9156
P3	279.40	259.13	**S3**	422.75	365.68	**C3**	229.9474	219.618
P4	*157.04*	*124.82*	**S4**	235.24	227.77			
P5	233.98	225.16	**S5**	218.46	208.95			
P6	240.07	210.62	**S6**	351.47	267.37			
P7	403.43	390.73	**S7**	*194.92*	*184.09*			
P8	431.53	424.28	**S8**	239.32	229.15			
P9	256.84	243.03	**S9**	287.69	269.65			
P10	277.26	278.45	**S10**	*148.48*	*143.41*			
P11	496.32	**	**S11**	201.45	*189.52*			
P12	**2143.92**	**1913.88**	**S12**	209.45	*199.44*			
P13	362.74	357.57	**S13**	*181.47*	*181.31*			
P14	405.22	392.09	**S14**	291.27	341.25			
P15	440.74	429.67	**S15**	*183.00*	*166.36*			
			S16	264.72	249.93			
			S17	268.01	261.58			
			S18	**	241.63			
			S19	303.92	281.25			
			S20	247.27	214.25			
Min	99.38	124.82		148.48	143.41		222.12	219.62
Max	2143.92	1913.88		488.61	444.02		275.81	265.92
Mean	437.15	421.03		269.93	251.90		242.63	242.77
S.t.d	468.44	422.79		87.02	75.30		23.68	23.15

** = Sample not measured due unavailability of borehole water

4.3 Detection of trace metals in water samples

The analytical results of As, Sb, Cd, Bi, Co and Cu were detected in low concentration between <2.0 – 3.8, 0.03 – 0.24, 0.02 – <0.09, 0.01 – <0.03, 0.24 – 1.57 and 1.02 – 58.58 µg/L respectively, during the course of this study. All samples complied with the recommended levels of these parameters (Appendix Table 4.6 and 4.7). Hence, these parameters do not pose any public health risk associated with consumption of sampled water.

4.3.1 Concentration of aluminum in water samples

In the selected school boreholes, the minimum and maximum Al concentrations detected ranged between 0.20 to 0.34 mg/L and 0.14 to 0.28 mg/L during the dry and wet season, respectively (Fig. 4.5). Meanwhile, water from the investigated private household boreholes has Al levels ranging from 0.15 to 0.30 mg/L and 0.18 to 0.76 mg/L in dry and wet season, respectively (Fig. 4.6). Furthermore, the communal borehole water concentration recorded Al concentrations between 0.15 to 0.20 mg/L and 0.18 to 0.23 mg/L in dry and wet season, respectively (Fig. 4.6). Almost all the boreholes (92.11%) comply with the standard set limit of SANS (2015) of 0.3 mg/L except S9, S11 in the dry season and P12 in the wet season. Aluminium concentration was observed to gradually increased during the wet season which oppose the observation of Mridul et al. (2009). The elevation of aluminium can be caused by dissolution of the element mainly from clays and other alumino-silicate minerals found in soils, sediments and rocks (Mridul et al., 2009). Care must be taken in drinking groundwater with high levels of Al because consumption could lead to accumulation of this metal in the body, hence causing long term health effect of Alzheimer's disease and renal failure in the consumers (Edokpayi *et al.,* 2014).

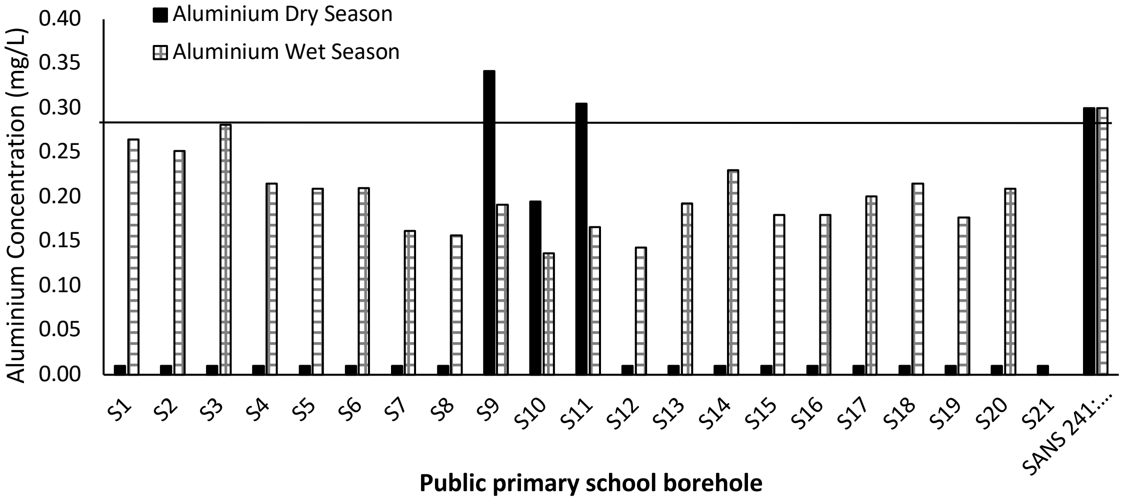


Figure 4.5: Aluminium concentrations of water samples taken from primary school boreholes during dry and wet season showing high concentration during wet period

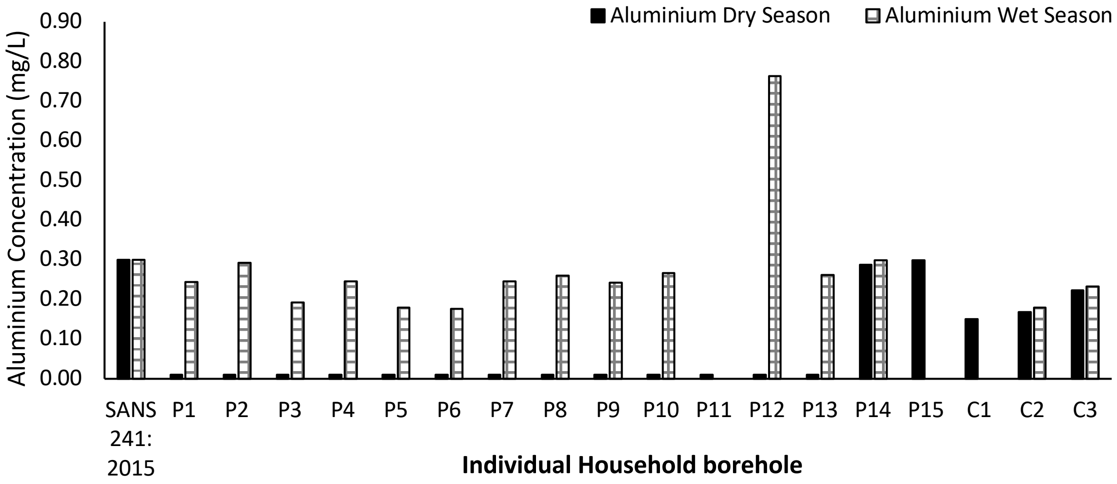


Figure 4.6: Aluminium concentrations for private boreholes in the study case area during dry and wet season

4.3.2 The detected Chromium (Cr) and Nickel (Ni) level in the collected water samples

The concentration of Cr in the primary school water samples ranged from 31.07 to 53.33 µg/L and 32.24 to 68.73 µg/L with a mean value of 36.65±4.40µg/L and 43.09±10.27 µg/L in dry and wet season, respectively (Table 4.8 and 4.9). 5.26% (n=19) and 30% (n=20) of school borehole water samples exceeded the acceptable limits of chromium concentration of 50 µg/L set by WHO (2015) and SANS 241(2015) (Table 4.8) in the dry and the wet season with the highest recorded values of 53.33 and 68.73 µg/L during dry and wet season, respectively for S12 and S17 (Table 4.8). In most borehole sites (63.16%), the concentration of Cr gradually increased in wet season as rainfall intensify. All groundwater samples collected from household and communal boreholes conformed to the standard guidelines (Appendix Table 4.7) apart from two samples (namely, P10 and C2) collected in wet season which was obtained with elevated concentration values of 64.61 µg/L and 72.84 µg/L, respectively.

Guo et al. (2020) reported similar findings of Cr concentration (10-86 µg/L) in Baiyangdian Basin, China. Edokpayi et al. (2018a) reported the range from 5 to 150 µg/L of Cr concentration in Muledane Village, South Africa throughout the study period. Seven of eight (87.5%) assessed borehole did not comply with the recommended water quality guidelines of <50 µg/L set by DWAF (1996) and WHO (2006).

In contrary to this study, Mubva (2019) reported low concentration of chromium in groundwater which was obtained at a range between 0.0 to 4.3 µg/L with estimated mean value of 0.7±0.9 µg/L in Ventersdrop, North West Province, South Africa. Cr is mostly found naturally in the environment as chromite ore ($FeCr_2O_4$) (Sharma et al., 2008; Al-Battashi et al., 2016). Though chromite is chemically inactive and insoluble in water, microbial interferences and geochemical processes could enhance Cr release in nature (Al-Battashi et al., 2016). Edokpayi et al. (2018a) suggested that high Cr concentration during the wet season could be due to high infiltration of water due to heavy rainfall and disposal of metal products around the study area which is similar to this study. Consumption of contaminated water with high Cr concentration (>50 µg/L) has possible risk of inducting gastrointestinal cancer following long-term exposure, DNA damage, slight nausea and undesirable taste in humans (DWAF, 1996; Kart et al., 2016).

The results of Ni concentration in all samples apart from Sample S3 (308.52 µg/L) collected during wet season (17.64 – 46.05 µg/L) complied with the acceptable limits of 500 (WHO, 2017) and 70 µg/L (SANS 241, 2015), (Table 4.8 and 4.9). In most samples, the concentration of Ni gradually decrease in wet season as rainfall intensify. This trend was in contrary to Cr, Al and Mg pattern

Vetrimurugan et al. (2017) reported Ni concentration at range between 90 to 170 µg/L with mean value of 120±20 µg/L which exceed the SANS standard guideline value (70 µg/L) for drinking purpose in Mhlathuze Catchment of KwaZulu-Natal Province, South Africa. Ni concentration is assumed toxic to certain flora and fauna with minimal effect on human (Vetrimurugan et al., 2017). Oakley and Korte (1996) identified certain stainless-steel materials as the source of nickel concentrations (8–395 µg/L and 1–5 mg/L) in groundwater wells in Arizona, USA. Similar case could be for groundwater from S3 site. Currently there is no published study conducted in the study area with comparable results concerning nickel concentration. The summary of statistic for these elements has been summarised in the Table 4.8 and 4.9 below.

Table 4.8 Statistical description of the concentration of trace metal (µg/L) in boreholes water within Makhado and Collins Chabane municipalities of Vhembe District , South Africa in Dry season.

Dry Season	**Schools**				**Households**				**Communal**				
Anion	**Min**	**Max**	**Mean**	**Std**	**Min**	**Max**	**Mean**	**Std**	**Min**	**Max**	**Mean**	**Std**	**SANS**
V	5.01	24.49	10.20	4.58	1.40	12.69	8.24	3.10	8.33	14.46	10.83	2.63	200
Cr	31.07	53.33	36.65	4.40	28.07	38.76	32.68	2.64	31.39	37.01	33.90	2.33	50
Mn	1.77	58.10	10.47	14.55	2.80	21.65	7.41	5.77	4.81	25.46	11.79	9.67	400
Ni	17.64	32.66	21.57	3.65	18.88	35.45	22.74	4.35	19.63	20.70	20.28	0.47	70
Cu	1.02	6.04	2.68	1.53	1.21	22.70	6.64	6.25	1.85	3.60	2.53	0.76	2000
Zn	15.63	68.90	27.65	11.76	21.72	99.80	43.50	25.76	17.42	36.82	26.55	7.96	5000
Hg	1.47	2.46	1.72	0.28	1.44	2.16	1.54	0.20	1.40	1.41	1.41	0.01	6
Pb	0.10	1.08	0.43	0.30	0.24	1.73	0.83	0.52	0.28	0.41	0.35	0.05	10
Fe	0.88	8.29	1.92	1.56	1.45	15.40	3.53	4.83	15.20	15.40	15.27	0.12	2000

Table 4.9 Statistical description of the concentration of trace metal (µg/L) in boreholes water within Makhado and Collins Chabane municipalities of Vhembe District , South Africa in wet season.

Wet Season	**Schools**				**Household**				**Communal**				
Anion	**Min**	**Max**	**Mean**	**Std**	**Min**	**Max**	**Mean**	**Std**	**Min**	**Max**	**Mean**	**Std**	**SANS**
V	5.59	23.59	11.51	5.17	3.93	13.81	7.69	2.88	0.42	24.53	12.47	12.05	200
Cr	32.24	68.73	43.09	10.27	27.46	64.61	37.35	11.14	31.94	72.84	52.39	20.45	50
Mn	2.15	26.51	7.64	6.65	1.63	16.54	4.70	4.18	17.17	20.27	18.72	1.55	400
Ni	19.00	308.53	40.22	61.97	16.35	29.40	21.87	4.39	20.99	40.21	30.60	9.61	70
Cu	1.15	58.58	7.37	13.52	2.63	19.56	9.20	6.15	5.55	20.35	12.95	7.40	2000
Zn	14.55	59.59	27.91	13.36	18.52	110.20	38.51	32.26	35.92	54.82	45.37	9.45	5000
Hg	1.14	1.66	1.35	0.12	1.09	5.43	2.29	1.21	1.19	1.41	1.30	0.11	6
Pb	0.15	2.87	0.55	0.57	0.21	4.14	1.23	1.20	0.33	3.28	1.80	1.47	10
Fe	15.20	15.50	15.34	0.10	15.10	20.60	15.74	1.41	15.20	15.30	15.25	0.07	2000

4.3.3 Presence of other trace elements in the investigated borehole water samples

Traces of Vanadium (V), Manganese (Mn) and Zinc (Zn) were detected in the borehole water samples. The results of V (1.4 – 24.49 µg/L), Mn (1.77 – 58.10 µg/L) and Zn (15.63 – 99.8 µg/L) were detected in low concentration for all borehole sites during the dry season, respectively (Table 4.8). Similarly, low levels of V (0.42 – 24.53 µg/L), Mn (1.63 – 26.51 µg/L) and Zn (14.55 – 110.20 µg/L) were also detected in wet season (Table 4.9). Similar study by Durowoju et al. (2020) reported low concentration level of V (3.21-18.36 µg/L), Mn (0.24-107.50 µg/L) and Zn (0.01-464.85 µg/L) throughout the assessment in Vhembe District, South Africa which complied with the SANS (2015) standard guideline values of 400 and 5000 µg/L for Mn and Zn respectively for drinking water.

4.3.4 Mercury (Hg) and lead (Pb)

Mercury (Hg) (1.09 – 5.43 µg/L), Pb (0.10 – 4.41 µg/L), were detected in concentrations that complied to the regulatory guidelines of 6 and 10 µg/L during this study. Although levels of Hg complied to the WHO (2015) standards some of the sites recorded values that exceeded the EPA (2018) guidelines of 2 µg/L. Previous works by Magara et al. (1989) and Durowoju et al. (2020) reported mercury concentration value of 5.5 µg/L and 6.11 µg/L in Izu Oshima Island (Japan) and Vhembe District, South Africa, respectively which exceeded the EPA (2018) limit of 2 µg/L. The elevation of Hg concentration could be due to underlying bedrock in a particular area (Barringer, et al., 2013; Leal-Acosta et a., 2018). Though the metal concentrations complied with the standard guidelines, the accumulation of these trace metals in the human body could result in adverse effects, considering that Hg and Pb are carcinogenic in nature (Durowoju et al., 2020). Lead is a general toxicant and a cumulative poison which can be found in groundwater (Pazand et al., 2018).

Lead concentration in this study was comparable with previous work by Vatandoost et al. (2018) which obtained Pb concentration at range between 0.0 and 9.0 µg/L in Anzali International Wetland, Iran. Though these assessments complied with WHO (2017) and SANS 241 (2015) set standard guideline limit of <10 µg/L for Pb concentration in drinking water, they exceed the EPA (2018) set permissible limit of zero Pb concentration. The source of lead concentration in groundwater could be dissolution from natural sources, application of phosphate fertilizers, herbicide and pesticides from household and farmlands, and household plumbing (Mahmood et al. 1998; Pazand et al., 2018; Rezaei et ai., 2019). The study area is far away from industrial activities. Hence, their contributions to trace metal levels are negligible. The continuing accumulation of trace metals in several parts of human body have been reported to show symptoms of mutagenic, carcinogenic, and teratogenic impacts (Rezaei et ai., 2019).

4.3.5 Iron (Fe)

The concentration of Fe in all water samples, ranged from 0.01 to 0.15 mg/L and 0.15 to 0.21 mg/L with estimated mean concentration of 0.04±0.05 mg/L and 0.15±0.01 mg/L in dry and wet season, respectively. These values are comparable with the values obtained from previous work by Edokpayi et al. (2018b) which reported Fe concentration range between 0.15 to 1.86 mg/L throughout the assessment. The reported values were within the recommended concentration of <2 mg/L (for chronic health) set by SANS 241 (2015). Meanwhile, this study contradicts this report in terms of aesthetic effect as it complied with both standard guidelines.

Groundwater associated with Fe concentration of <0.3 mg/L could have a minor effect on taste and slight staining of clothes if used for domestic purpose. Fe concentration seems to be more in wet season than in dry season apart from communal borehole site P15 and C3. Moreover, S11 and P4 had Fe concentration higher than other sites in dry and wet season, respectively. This could be as a result of Fe leaching from sewer pipes and disposed metals on land during heavy rainfall events. Moreover, dissolution of Iron due to oxidation and change in pH levels could increase Fe concentration in groundwater (Asare-Donkor et al., 2016; Edokpayi et al, 2018a). Borehole site P15 (Household) and C3 (communal) site maintain concentration stability throughout the assessment which suggest that these boreholes were not affected by seasonal variability (Table 4.8 and 4.9).

4.4 Factors controlling Groundwater chemistry

The Gibbs diagram of the water samples (Fig. 4.7 - 4.10) clearly shows that the majority of samples collected from selected primary school, individual household and communal boreholes assembled at the region of rock dominance.

The geochemical facies evaluation of groundwater shows that most of the groundwater samples are of Ca-Mg-HCO_3 type which correlate with the findings of Edmunds et al., (1987) as groundwater is dominated by carbonate rocks (Edmunds et al., 1987). The piper diagrams presented in Figure 4.11 and 4.12 clearly show the dominance of alkaline earth metal (Ca^{2+} and $Mg^{2+)}$ over alkali metals (Na^+ and K^+). Meanwhile, the weak acids (CO_3^{2-} and HCO_3^-) dominated the strong acids (Cl^- and SO_4^{2-}) which alert for temporary hardness of the water. As water consisting of dissolved carbon dioxide passes through minerals such as magnesite (magnesium carbonate), limestone or other calcium carbonate, it dissolves part of the calcium/magnesium carbonate and becomes richer in bicarbonate. Though most groundwater samples assembled in weathering and rock dominance region, sample P2 and P12 fell under precipitation dominance and dissolution of evaporate minerals region, respectively in dry season (Sahib *et al*., 2016). Gibbs diagram suggest a precipitation dominance of sample P2 which could be due to water rock interaction, fresh or water recharge from precipitation.

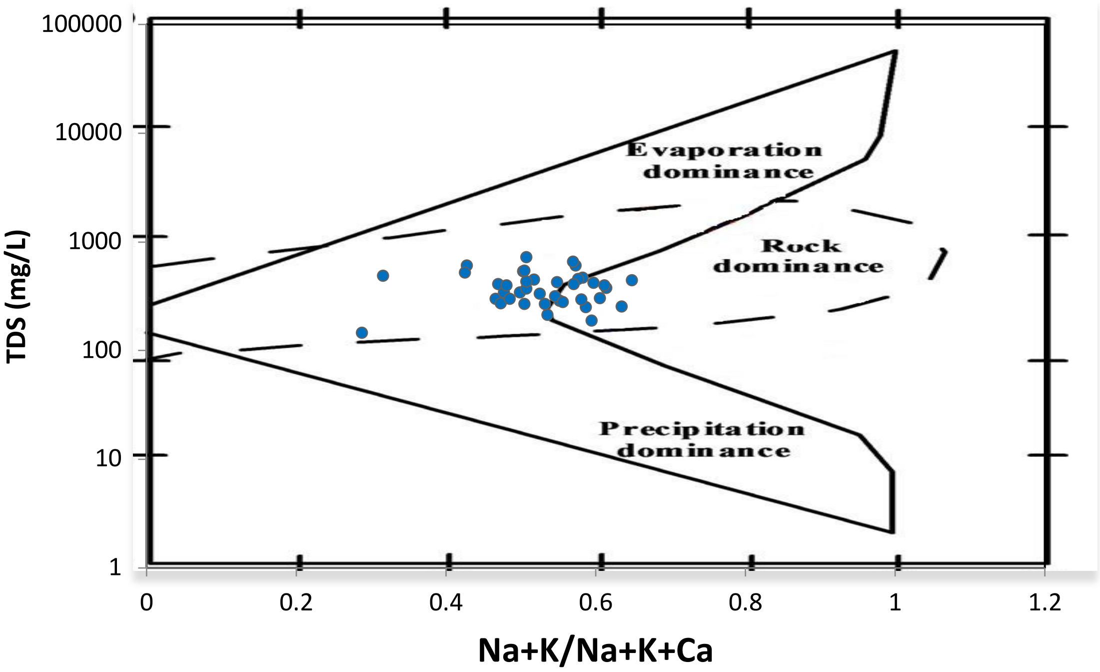


Figure 4.7: Gibbs plot presenting the dominant cation mineralisation process of groundwater in selected primary schools in Makhado and Collins Chabane municipal

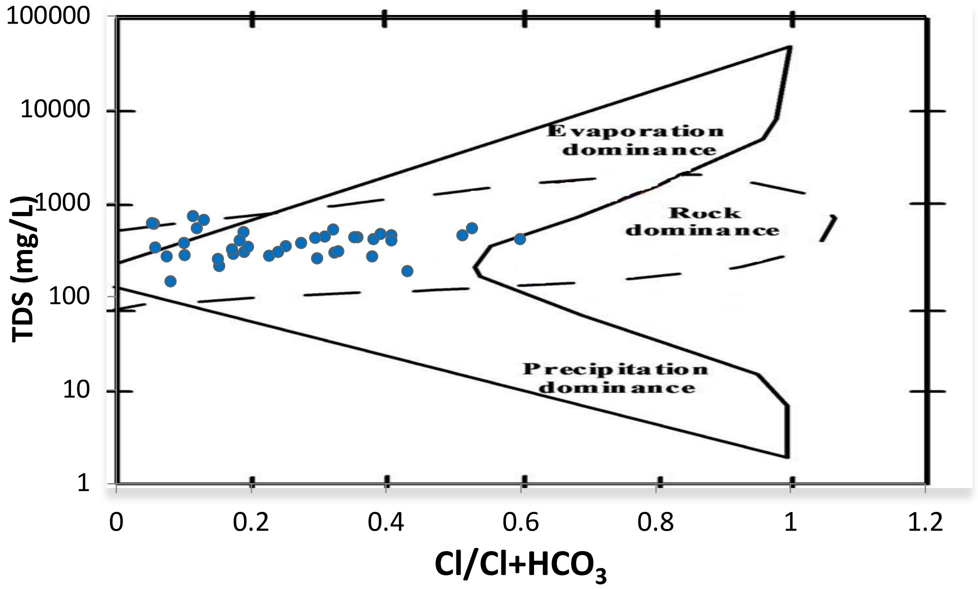


Figure 4.8: Gibbs plot presenting dominant anion mineralisation process of groundwater in selected primary schools within Makhado and Collins Chabane Municipality

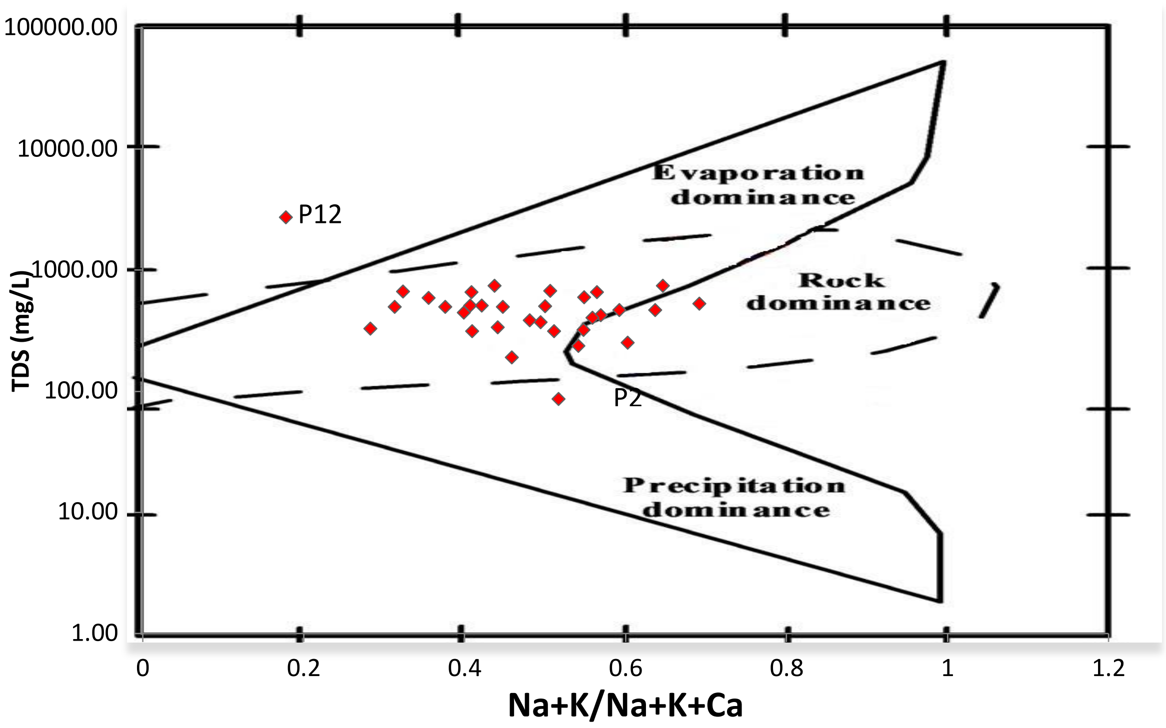


Figure 4.9: Gibbs plot presenting dominant cation mineralisation process of groundwater in selected individual household and communal boreholes within Makhado and Collins Chabane municipality

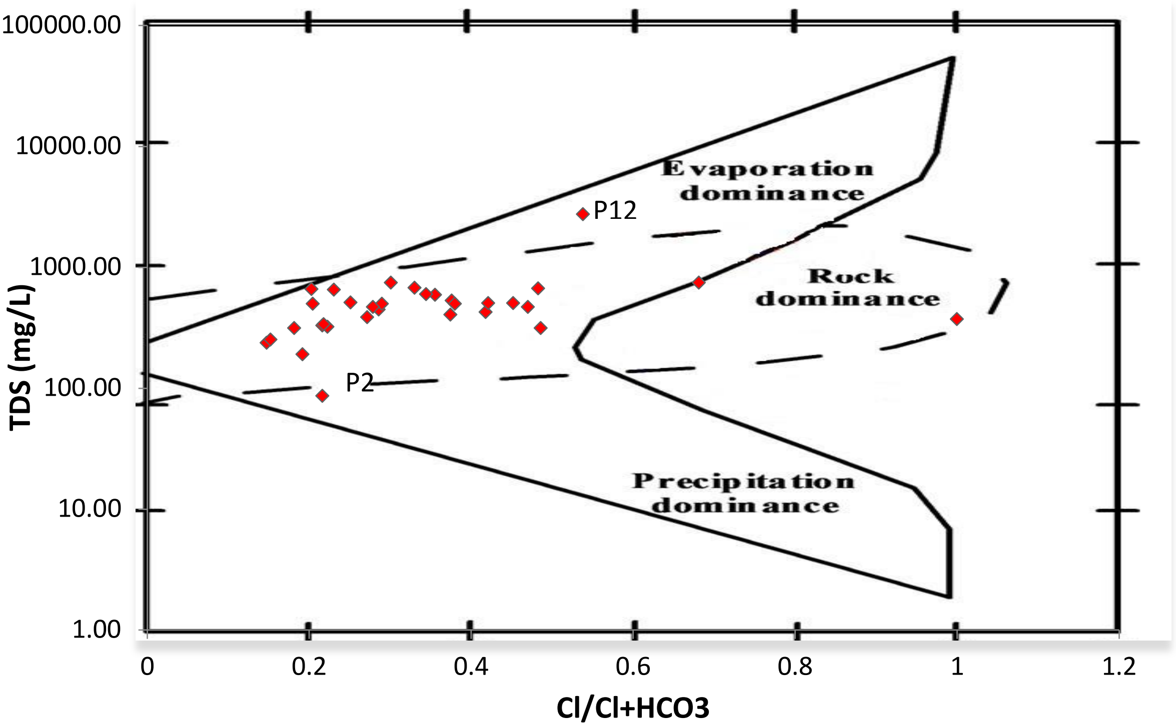
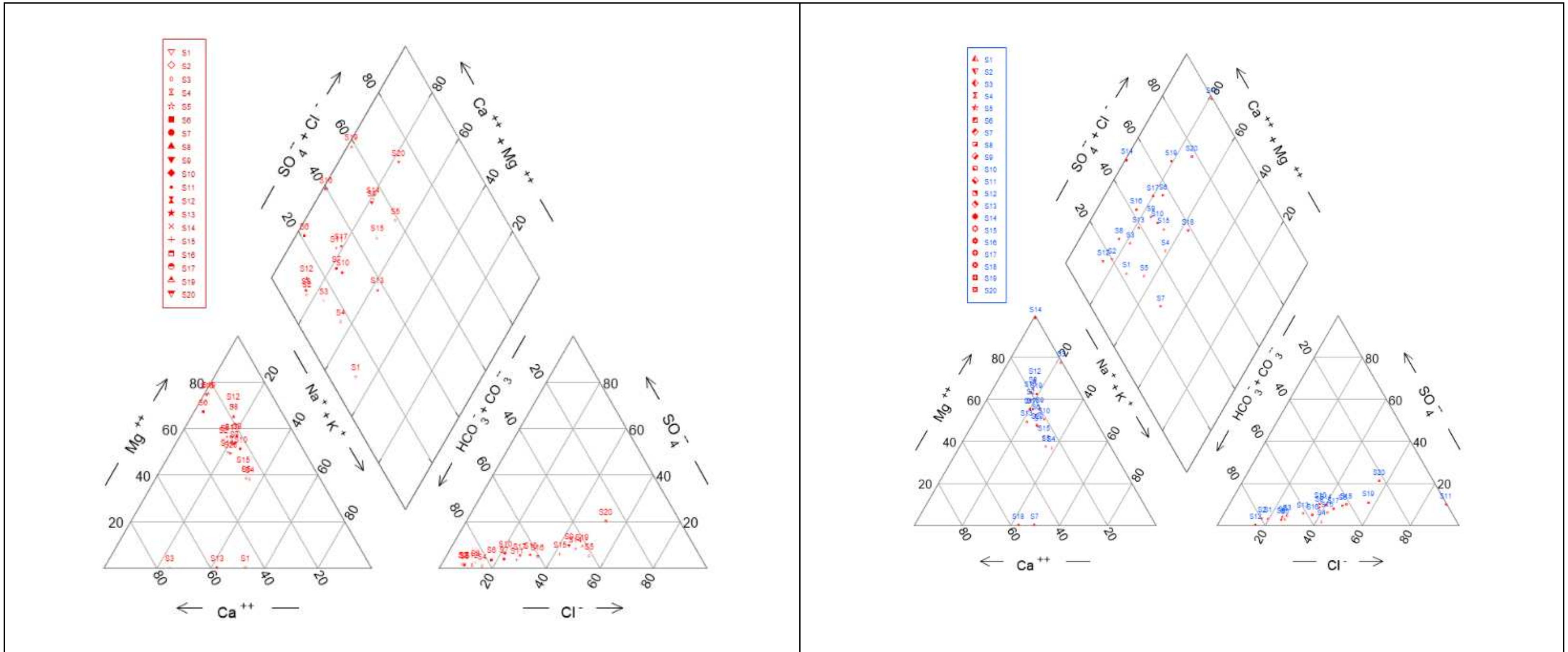


Figure 4.10: Gibbs plot showing the dominant anion mineralisation process of groundwater in from household and communal boreholes

One common evolution of groundwater in carbonate aquifers moves from Ca-HCO_3 type waters to Ca-Mg HCO_3-SO_4 type waters (Zhang *et al.*, 2020). Such evolution occurs on the left sides of the Piper diagram triangles and in the upper part of the diamond (Hanshaw and Back, 1979). Still, it cannot be witnessed on Gibbs diagram as the variation is caused by Ca-Mg ratio and HCO_3^--SO_4 ratios while, the Ca-Na and Cl-HCO_3^-ratios remain unchanged.

Further evolution of groundwater chemistry (changes to the type and salinity of the groundwater) may occur due to redox-controlled reactions, the interaction of different groundwater types along the flow paths, cross-formational flows and exchange with aquitards, and by groundwater recharge from surface waters with higher salinities (Marandi and Shand, 2018). The piper plot classified groundwater samples as according to their geochemistry type (Fig. 4:11 and Fig. 4:12). The summary of groundwater water type is presented in Figure 4.13. In comparison with all groundwater sample collected from schools in both wet and dry season, 36.84% (n=19) of groundwater samples (S1-3, S7-8, S12 and S16) had Mg-HCO_3 water type.

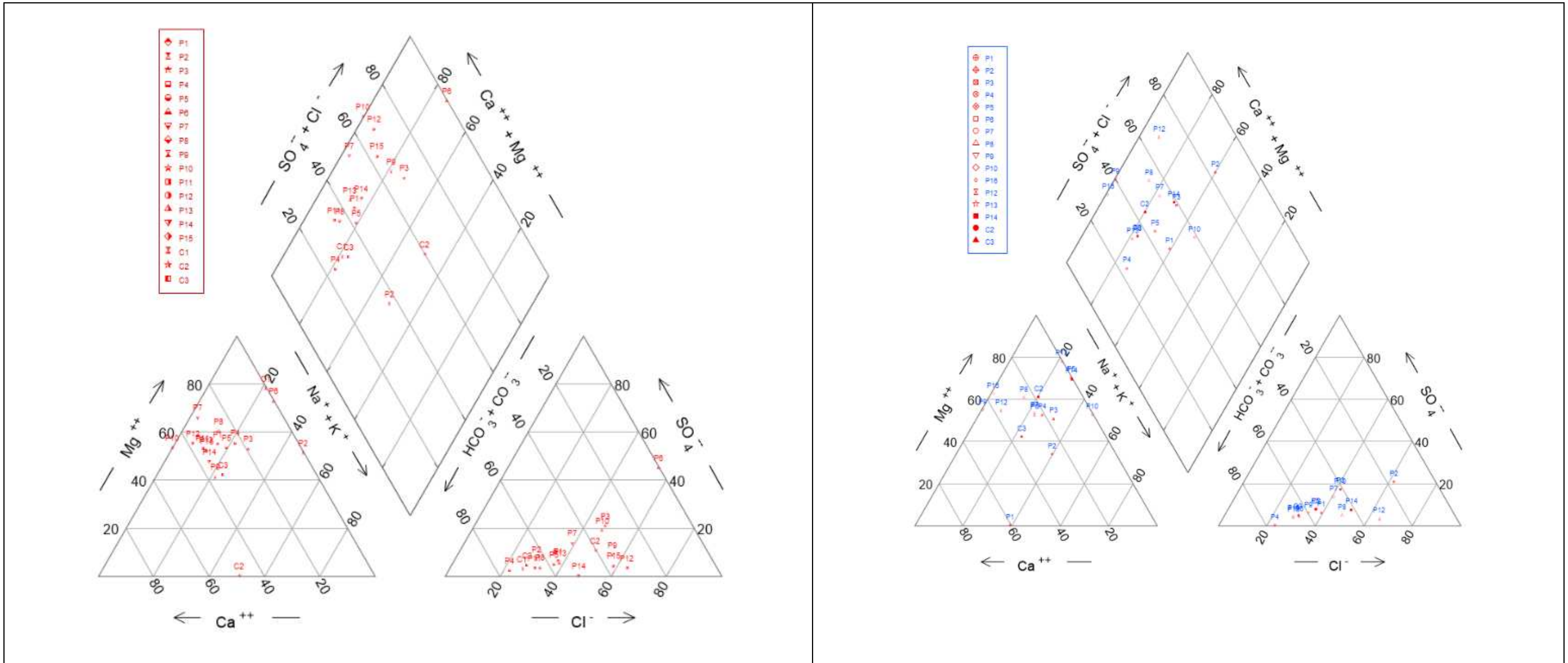
Meanwhile, 21.05% (n=19) of groundwater samples collected from schools (S13-15, and S15) had Mg-Cl water type throughout this study. Samples from borehole site P1, P10, P12, P14 and C2 were detected with Mg-Cl water type throughout the assessment. Only Communal borehole site C3 have been categorised as Mg-HCO_3 water type in both wet and dry season. While the P3 and P7 water samples were obtained with Mg-NO_3 water type throughout the study period. The chemical dominance in school boreholes followed a trend in decreasing order of Mg-HCO_3> Mg-Cl >Na-Cl=Ca-Cl, while for individual household and communal borehole were found in order of Mg-Cl> Mg-HCO_3= Mg-NO_3> Na-NO_3=Ca-HCO_3 and Mg-HCO_3> Mg-Cl respectively. Generally, sample collected from primary school and communal boreholes was dominated by Mg-HCO_3, meanwhile private household, was dominated by Mg-Cl water type (Fig. 4:13). Considering the chemical dominance of groundwater chemistry of Collins Chabane and Makhado municipality, the trend in decreasing order were Mg-NO_3> Mg-HCO_3> Mg-Cl> Na-Cl> Ca-Cl= Na-NO_3> Ca-HCO (Fig. 19d).



a) Piper plot presenting dominant ions in dry season

b) Piper plot presenting dominant ions during wet season

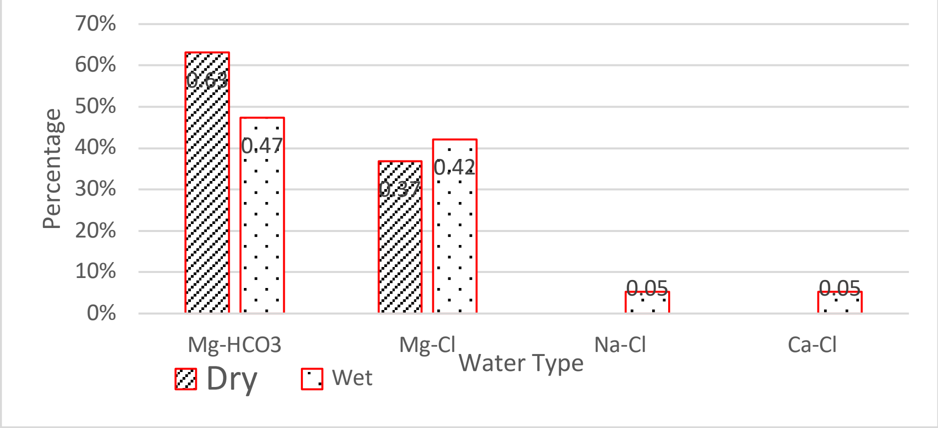
Figure 4.11: Piper plot presenting dominant ions in the selected school groundwater samples



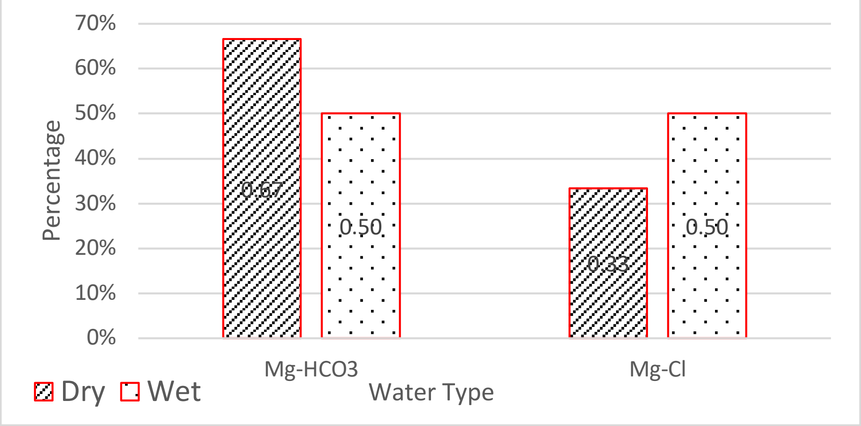
a) Piper plot presenting dominant ions during dry season

b) Piper plot presenting dominant ions during wet season

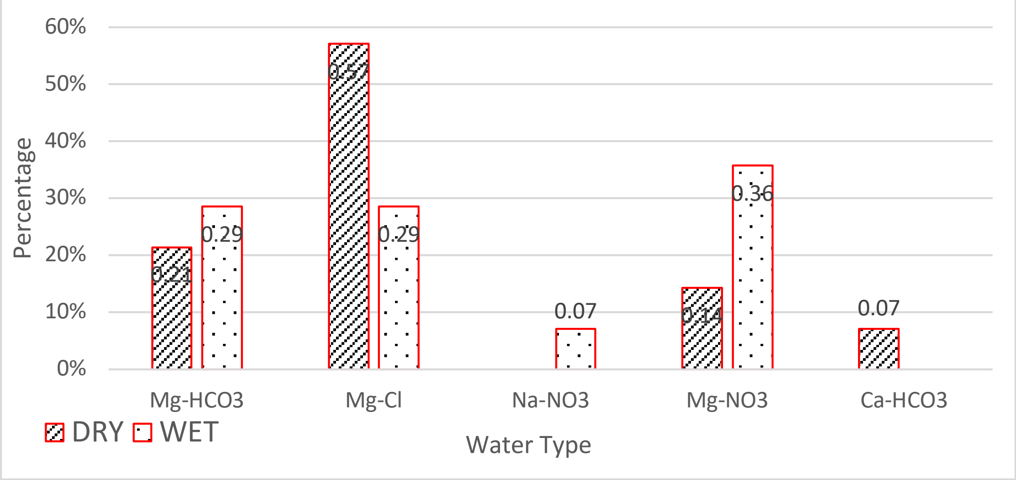
Figure 4.12: Piper plot presenting dominant ions in the selected household and communal groundwater samples



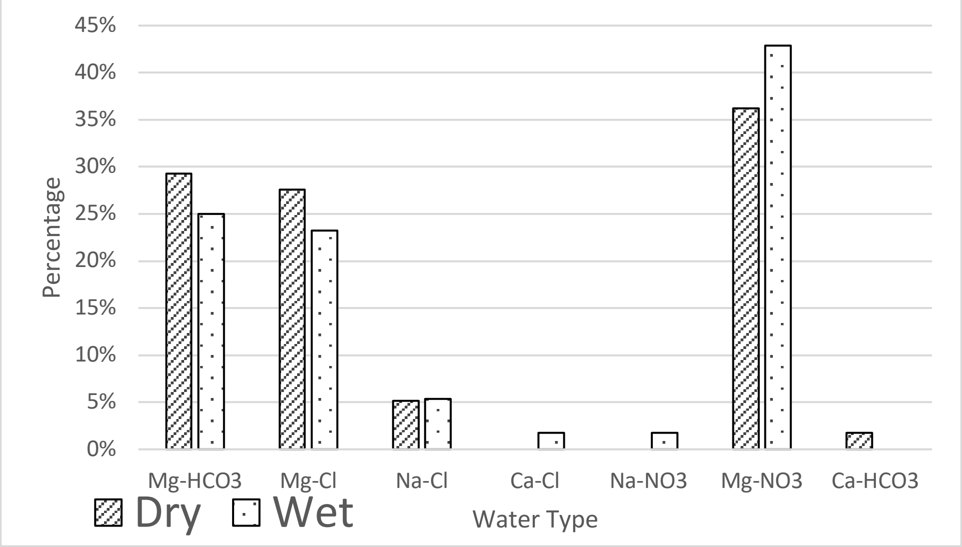
a) Groundwater chemistry of schools in Collins Chabane and Makhado municipality



b) Groundwater chemistry of communal in Collins Chabane and Makhado municipality



c) Groundwater chemistry of household in Collins Chabane and Makhado municipality



d) Overall groundwater chemistry of Collins Chabane and Makhado municipality

Figure 4.13: Groundwater chemistry of selected individual and communal boreholes in Vhembe district

4.5 Water quality index

This section intend to calculate the groundwater quality index (WQI) of Collins Chabane and Makhado municipality in order to assess its suitability for drinking purpose and domestic use. For calculating WQI, 21 parameters were considered (Table 4:10).

Table 4:10: Descriptive statistics for observed water quality data for primary school boreholes for dry and wet season

		Water Quality Variables /Chemical range for primary School boreholes						
		Dry season			Wet Season			
Parameters	W_i	Min	Max	Mean	Min	Max	Mean	Standard (mg/L)
pH	0.064	6.77	7.75	7.28	6.84	7.95	7.43	5-9.7
E C (mS/m)	0.032	19	93.2	55.10476	35.8	90.1	56.95	170
Cl^- (Chloride)	0.045	14.12	68.58	41.07143	14.7	68.96	42.5805	250 (WHO, 2008)
NO_3^-	0.080	7.02	111.14	44.67714	6.92	120.4	47.7355	50 (WHO, 2005)
F^-	0.080	0.03	2.16	0.374762	0.03	2.03	0.3365	1.5
SO_4^{-2}	0.064	0.55	32.91	9.414762	2	29.7	9.9745	500
HCO_3^-	0.016	57.34	911.95	253.0048	39.65	381.25	130.1435	600 (WHO, 1997)
Ca	0.048	16.1	75.3	34.28571	14.4	63	31.385	200 (WHO, 2011)
Mg	0.043	8.48	79.3	41.47524	24.7	78.9	42.14	50 (WHO, 2015)
K	0.032	0.58	10.7	3.668095	1.58	12.8	4.0215	12 (WHO, 1997)
Na	0.064	9.57	68.4	30.09857	15.3	65.1	32.705	5-9.7
Total Hardness	0.016	148.48	488.61	269.93	143.41	444.02	251.90	500
Mn (µg/L)	0.032	1.77	58.10	10.47	2.15	26.51	7.64	400
Cr (µg/L)	0.080	31.07	53.33	36.65	32.24	68.73	43.09	50
Co (µg/L)	0.032	0.30	0.72	0.42	2.80	25.46	8.63	500
Ni (µg/L)	0.032	17.64	32.66	21.57	19.00	308.53	40.22	70
Cu (µg/L)	0.032	1.02	6.04	2.68	1.15	58.58	7.37	2000
Zn (µg/L)	0.016	15.63	68.90	27.65	14.55	59.59	27.91	5000
Hg (µg/L)	0.080	1.47	2.46	1.72	1.14	1.66	1.35	6
Pb (µg/L)	0.080	0.10	1.08	0.43	0.15	2.87	0.55	10
Fe (µg/L)	0.032	0.88	8.29	1.92	15.20	15.50	15.34	2000
$\sum W_i$	1.000							

pH, EC, Cl^-, NO_3^-, F^- , SO_4^{-2}, HCO_3^-, Ca, Mg, K and Na were taken into consideration for household and communal samples while an additional of 9 trace metals (Cr, Mn, Co, Ni, Cu, Zn, Hg, Pb, Fe) and total hardness as $CaCO_3$ were considered in school samples. Some trace elements could not be analysed from household and communal samples due inadequate water samples. Majority of the parameters were within the permissible limit according to WHO (1997). The concentration of NO_3^- in 52.06% of samples is above the permissible limit laid down by WHO (2005).

The WQI value of the selected schools (50-103 and 25-101), household (26-485 and 21-442) and communal (35-57 and 50-56) borehole during dry and wet season respectively fell between the excellent to poor, excellent to unsuitable and excellent to good water based on the parameters used, respectively. The observation of school and communal borehole water samples was similar to the study by Ram et al. (2021) in Bundelkhand massif (India) with WQI range between 4.75 to 115.93 (excellent to poor water category) throughout the assessment.

A category of excellent, good and poor water was obtained in 41.03 (n=39), 53.85(n=39) and 5.13% (n=39) of school water samples during the entire study period, respectively (Fig. 4.14). A good class of water was dominant by 40% (n=15) and 50% (n=14) in household water samples respectively in dry season and wet season. Moreover, low percentage (13.33% and 7.14%) of unsuitable water class were observed from household in dry and wet season, respectively (Fig. 4.15).

Communal borehole showed excellent performance by displaying 66.67% (n=3) and 50.00% (n=2) of excellent water class during dry and wet season. Meanwhile good class has been observed in 33.33% and 50.00% in communal sample during dry and wet season, respectively.

Highest values of WQI were observed in P6 (485) in dry season and P12 (444 and 442) during dry and wet season, respectively. These values of water quality index suggest that groundwater samples collected from individual household (P6 and P12) were extremely not suitable for drinking and agricultural purposes at that period. This is due to high concentration of measured nitrates (P6, SI=432; and P12, SI=238), fluoride (P12, SI=12) and magnesium (P6, SI=6; and P12, SI=47), fluoride (P12, SI=12) and calcium (P6, SI=8 and P12, SI=92) which makes the groundwater inadmissible for drinking purpose in dry season.

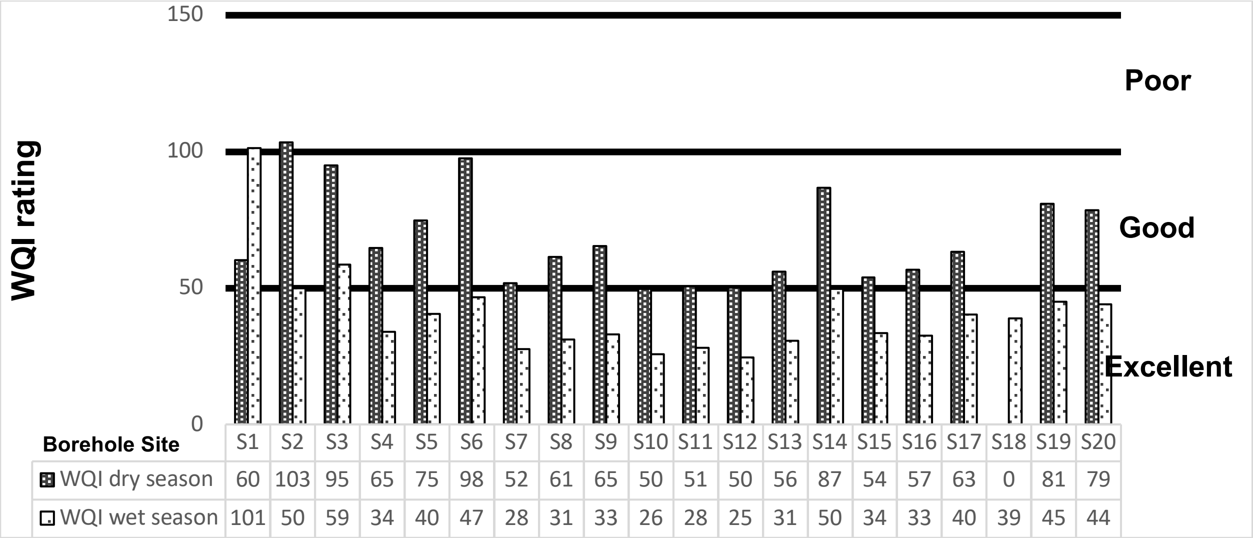
Table 4.11: Descriptive statistics for observed water quality data for Private household and communal Borehole for a for dry and wet period

		Private and Communal Borehole						
		Dry season			Wet Season			Standard (mg/L)
Parameters	W_i	Min	Max	Mean	Min	Max	Mean	(SANS 241:2015)
pH	0.112676	6.94	8.27	7.30	6.90	10.87	7.58	5-9.7
EC (mS/m)	0.056338	25.20	825.00	124.58	33.40	98.70	67.26	170
Cl^- (Chloride)	0.078873	19.16	646.64	87.62	15.13	690.00	99.57	250 WHO (2008)
NO_3^-	0.140845	2.03	1532.00	**203.89**	0.06	924.74	149.49	50 (WHO, 2005)
F^-	0.140845	0.03	1.24	0.49	0.03	1.46	0.52	1.5
SO_4^{-2}	0.112676	2.68	46.30	18.05	0.01	48.98	19.89	500
HCO_3^-	0.028169	0.00	555.71	146.77	51.24	579.50	164.05	600 WHO (1997)
Ca	0.084507	18.20	349.00	60.74	14.20	308.00	58.82	200 (WHO, 2011)
Mg	0.076056	11.40	309.00	61.45	21.70	278.00	61.60	50 WHO (2015)
K	0.056338	0.49	12.50	4.88	0.50	12.60	4.91	12 WHO (1997)
Na	0.112676	17.80	67.90	31.46	19.80	97.80	44.44	200
$\sum W_i$	1.000							

NO_3 is the major pollutant factor responsible for the lowest WQI scores for stations P6 and P12 with concentrations of 1532, 204 and 846 mg/L, respectively in dry season. Meanwhile the lowest WQI scores were obtained from P6 (SI=19),) and P12 (SI=260), with detected concentration of 66.29 and 925 mg/L, respectively in wet season. According to this study methodology (see Chapter 3: Calculation of WQI and Table 4.10 and 11), WQI standards have been categorised into five classes: 1 for Excellent (< 50), 2 for Good (<50 to 100), 3 for poor (>100 - 200), 4 for very poor (>200- 300) and 5 for unsuitable for drinking (> 300) (Sahu and Sikdar, 2008; Singh et al., 2016). The communal borehole water fell under class 1 and 2 which is poor and good with 56 and 50 WQI values for C2 and C3 boreholes respectively, during wet season, while site C1, C2 and C3 was obtained with 35, 57 and 46 WQI values during dry season (Fig. 4.21), respectively. Generally, all groundwater samples were suitable for domestic use apart from individual household P6 in dry season and P12 throughout the study period (Fig. 4.15).

Samples P2 and P11 recorded WQI values of 107 and 106 which falls under poor category during wet and dry season, respectively. Household site P7, P8, P11 and P12 (107 - 444) fell under poor to unsuitable category throughout the assessment. The conditions for schools vary with season whereas for some private boreholes did not varies with season except for P2 and P6. Several borehole sites (94,74%, n=19) from school had high WQI in dry season compared to wet season apart from S1. Meanwhile household borehole sites (64.28%, n=14) had high WQI in wet season as compared to dry season. Several concentrations of metals and anions are transported with water into the groundwater in dry season during irrigation and heavy rain in wet season. Several household boreholes are located not far away from concentrated livestock without slurry storage facility and proper manure storage which is suggested to be a point source of pollutant in this study (Zhou, 2015).

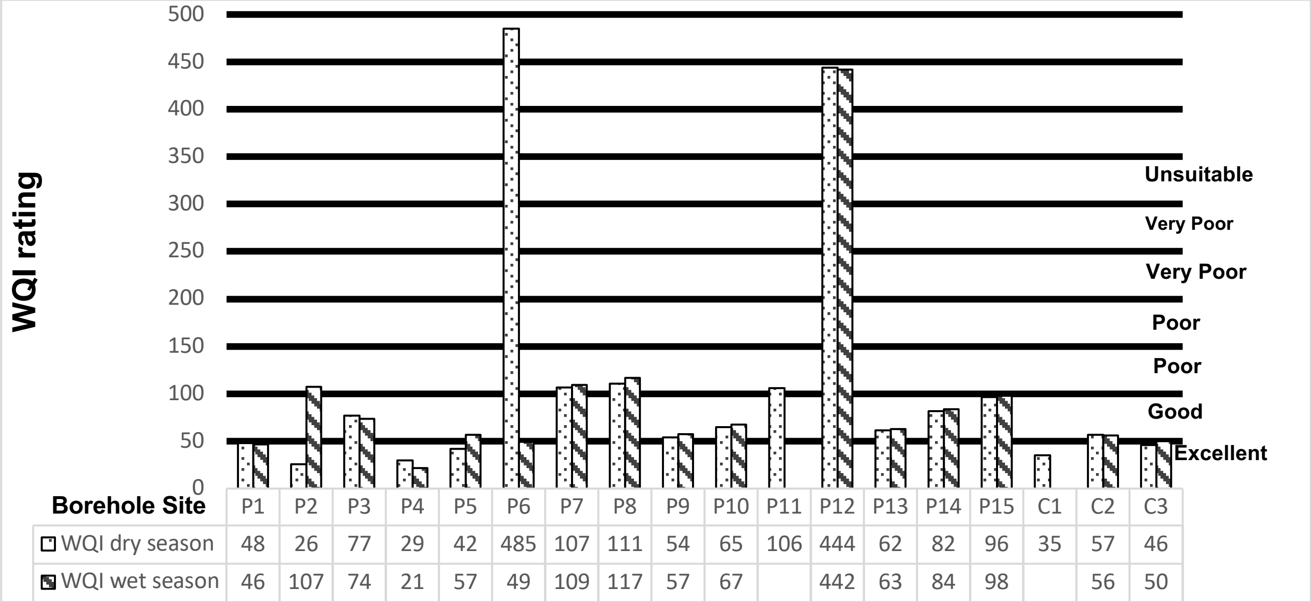
In this study, high levels of NO_3^- were recorded in dry periods which contradict with the finding of Banda *et al*. (2020). The correlation between the means of Nitrate concentration (P(F<=f) = 0.02) collected from household in dry and wet were statistically significant since P(F<=f) value were less than α (0.05) significant level. Nitrate is the principal form of nitrogen which is soluble in water. It easily percolates through soil pores to the ground-water table. Therefore, the application of nitrogen substances to the land surface every year, can persist nitrate into groundwater for decades and accumulate to high levels.



Borehole Site	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20
▩ WQI dry season	60	103	95	65	75	98	52	61	65	50	51	50	56	87	54	57	63	0	81	79
☐ WQI wet season	101	50	59	34	40	47	28	31	33	26	28	25	31	50	34	33	40	39	45	44

Figure 4.14: The classification of borehole sites from selected schools in Makhado and Collins Chabane municipality in dry and wet season

The source of contamination might be anthropogenic activities, especially inorganic fertilizer which includes lawn fertilizers, septic systems, improper pit latrine toilet, and domestic animals in residential area (animal manure) among others. In most primary schools, there is a small piece of agricultural land within the vicinity of borehole, application of animal manure and inorganic fertilizers could be the cause of high nitrates concentration in groundwater. NO_3^- is a naturally occurring ion (Fan, 2011; Serio *et al.,* 2018) that is widespread and is regarded as the most significant contaminant in water (Espejo-Herrera, 2015; Sadler, 2016).



Borehole Site	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	C1	C2	C3
☐ WQI dry season	48	26	77	29	42	485	107	111	54	65	106	444	62	82	96	35	57	46
▨ WQI wet season	46	107	74	21	57	49	109	117	57	67		442	63	84	98		56	50

Figure 4.15: The classification of borehole samples from individual and communal sites in Makhado and Collins Chabane municipality in dry and wet season.

Nitrate is a low-toxicity compound in nature, nonetheless when endogenously transformed to nitrite (NO_2), it turns into a toxic compound in the aquatic environment and for human health (Fan, 2011; Serio *et al*., 2018). Thus, there should be support for systematic water quality monitoring to detect water quality trends over some space and time (Shah and Joshi, 2017). The mineral composition as suggested by speciation modelling and the alkaline nature of groundwater supports the chemical reaction for fluoride enrichment through weathering (Molekoa *et al*., 2019).

The conditions for schools varies with season whereas for some (71.42%, n= 14) private boreholes did not varies with season. In general, the computed WQI values suggest that 83.57% (n=73) of the water samples fell into the good and excellent water categories whereas the few samples (16.43%, n=73) stood in the poor to unsuitable categories which implies that the water quality may further deteriorate if timely actions for their management are not taken into consideration. These findings are similar with the WQI results values of Molekoa *et al*. (2019) whereby few groundwater samples (20%, n =12) were within the category of poor to very poor with 80% majority of excellent to good. In general, the samples collected from school and communal water samples ranged from excellent (40.91%, n= 44) to good (54.55%, n= 44) whereas private household ranged from Excellent to Unsuitable. The Presented WQI only considered the chemical parameters as this seems to be a norm in most studies (Olasoji et al., 2019). However, microbiological parameters could change the perceived good to excellent water category in other samples assessed in this study since similar studies reported microbial parameters as threat to human health (Edokpayi et al., 2018a; Edokpayi et al., 2018b; Olasoji *et al*., 2019; Odiyo *et al*., 2020; Madilonga *et al*, 2021).

4.6 Microbiological analysis

4.6.1 Total Coliform

During the study assessment, the total coliforms during the dry and the wet seasons were analysed for groundwater samples collected from school (2-850 cfu/100 mL and 14-1000 cfu/100 mL), household (0-1280 cfu/100 mL and 0->1000 cfu/100 mL) and communal borehole (2-224 cfu/100 mL and 0-15 cfu/100 mL) (Table 4. 11). Based on total coliform count, water quality is very poor because the majority of school (94.44% and 85.00%), household (60.00% and 76.92%) and communal borehole (66.67% and 50.00%) did not fall within the permissible limits during dry and wet season, respectively. Based on previous study, most boreholes within the vicinity of pit latrine toilet are confirmed to yield water supply with microbial contamination (Holland, 2011) due to infiltration of water from sanitary facilities (pit latrine and septic tanks) (Mzuga *et al*., 1998; Odiyo and Makungo, 2018). All samples collected from school boreholes in the dry season did not conform to SANS 241 standard of <10 cfu/100 mL count for total coliform.

4.6.2 Escherichia coli (*E. coli*)

E. coli is considered the most suitable indicator of fecal contamination and occurs in high numbers in human and animal wastes, sewage and water subject to recent fecal pollution (WHO, 2011). During the study assessment, the *E. coli* were analysed for groundwater samples collected from school (0-65 cfu/100 mL and 0 ->1000 cfu/100 mL), household (0-76 cfu/100 mL count and 0 -17/100 mL) and communal borehole (1-2 cfu/100 mL and 0-0 cfu/100 mL) during dry and wet season, respectively (Table 4.12). Based on *E. coli* count, water quality of school (27.78% and 10.00%), household (6.67% and 7.69%) and communal borehole sample (100.00% and 0.00%) did not fall within the permissible limits during dry and wet season, respectively. The majority of samples (91.43%, n=35) complied with SANS 241 (2015) and WHO (2015) standard guideline value of 0 cfu/100 mL count apart from sample collected from S12 (190), S17 (>1000) and P2 (17 cfu/100 mL) site in wet season, respectively.

Meanwhile in dry season, high counts of *E.coli* (15-65 and 76 cfu/100 mL) were observed in 7.69 and 3.345% of school and household borehole samples, respectively. This suggests for high possibilities of infection related to *E. coli* contamination from drinking water during dry season in the study area more especially to school learners. Lower values for *E.coli* count were also observed in C1 (2 cfu/100 mL), C2 (2 cfu/100 mL) and C3 (1 cfu/100 mL) in dry season. The recommended standard value for *E. coli* count by SANS 241 is 0 cfu/100 mL for drinking water purposes (SANS, 2015). Though these values are low, they are not acceptable in drinking water (WHO, 2015). Previous study by Edokpayi et al. (2018b) indicated the occurrence of diarrhea in groundwater associated with *E. coli* contamination in Vhembe District Municipality. This gives an alarm to conclude that *E.coli* is major threat to the health of people residing in Vhembe District which include the community of this study area

The results show that *E. coli* levels in school water samples, increases from dry to wet season which is not the case on household and communal borehole. The sources of contamination could be from anthropogenic sources such as poorly managed and constructed pit latrine toilets and waste from concentrated livestock, improper positioning of individual sewage septic tanks, which must have led to percolation/infiltration of untreated household wastewater, and graveyards (Kumar et al., 2013, Zhou, 2015; Manyi-Loh et al., 2016; Edokpayi et al., 2018b; Ayilara et al., 2020).

These findings correspond to the study conducted by Esterhuizen *et al*. (2015) and Odiyo *et al.,* (2020) for the groundwater samples collected from 37 dairy farms in the Free State Province of South Africa and 10 public schools in Vhuronga 1, South Africa, respectively.

The F-test statistical analysis have been performed to test the mean difference of total coliform and *E.coli* between dry and wet seasons. The statistical description of F-test have been shown in Table 4.13. There was no statistical difference between the means of total coliform in household water samples collected in dry and wet season with p-value of 0.27 while, *E.coli* had statistical difference between sample means. The correlation between the means of *E.coli* (P(F<=f) = 5.74E-03) and total coliform (P(F<=f) = 1.17E-15) in dry and wet were statistically significant since P(F<=f) were less than α (0.05) significant level.

4.7 Correlation analysis

4.7.1 Correlation summary among physicochemical parameters groundwater samples

A correlation between physical parameters with ions were performed for school samples in dry and wet season. A strong positive significant correlation of EC with TDS, Salinity and Total hardness (TH) (r=0.805, 0.848, 707; p=, respectively) were observed in dry season while in wet season, EC had a very strong positive correlation with TDS, Salinity and Total hardness (TH) (1.00, 0.914, 0.935, respectively). Similar findings were reported by Zainol et al. (2021)

A direct proportionality occurs between the correlation of TDS and EC because EC is a measure of ionic charge in water. Meanwhile, TDS measures the summation of ions, cations, and anions in water. Hence, TDS could be useful to suggest the character of both salinity and EC of groundwater (Zainol et al., 2021). A direct proportionality between the correlation of TDS, salinity and EC suggests that an increase or decrease of one give rise or fall to another.

A positive correlation between EC with anions such as Cl^-, NO_3^-, F-, and HCO_3^- (0.691 and 0.604, 0.7 and 0.533, 0.557 and 0.732, 0.561 and 0.73, respectively), were shown in Table 4.14 in dry and wet season respectively. The relationship between EC with Cl ion, TDS and TH was statistically significant in both dry and wet season (P= 0.001 and 0.005, 1.87E-05 and 2.43E-142, 0.001 and 1.48E-09, respectively).

Meanwhile Salinity had a strong significant correlation with TDS, HCO_3^- and TH (0.80-0.91, 0.69-0.70, 0.80-0.86, respectively) in dry and wet period at 0.01 significant level since $p < 0.01$. The correlation of HCO_3^- ions with these parameters suggests that this ion often have an influence on the behavior of these parameters. pH exhibited a moderate relationship with TH (r= 0.514 and 0.451, P= 0.024 and 0.046), in dry and wet season, respectively. The inter-relationship among EC and total hardness with other ions and metals in household samples have been determined through correlation analysis as displayed on Table 4.15.

Table 4.12: The levels of Total coliforms and *E. coli* detected in the primary schools and individual household borehole during the course of the study within Makhado and Collins Chabane municipality.

	Wet		Dry			Wet		Dry			Wet	Dry	Wet	Dry
SN	E.	Total	E. coli	Total		E. coli	Total	E. coli	Total		E. coli	Total	E. coli	Total
S1	0	103	0	2	P1	0	0	0	375	C1	**	**	2	53
S2	0	504	0	132	P2	17	155	0	40	C2	0	15	2	2
S3	0	61	0	83	P3	0	284	0	0	C3	0	0	1	224
S4	0	302	0	49	P4	0	140	0	0					
S5	0	56,5	0	28	P5	0	300	0	0					
S6	0	500	0	55	P6	0	43	0	101					
S7	0	222	0	850	P7	0	64	0	4					
S8	0	>1000	0	82	P8	0	0	0	0					
S9	0	268	0	66	P9	0	620	0	170					
S10	0	241	15	61	P10	0	24	0	186					
S11	0	>1000	8	42	P11	0	>1000	0	140					
S12	190	490	65	71	P12	**	**	0	35					
S13	0	40	**	**	P13	0	0	76	156					
S14	0	350	0	37	P14	0	956	0	1280					
S15	0	895	0	17	P15	**	**	0	0					
S16	0	29	1	22										
S17	>1000	>1000	0	25										
S18	0	14	10	200										
S19	0	83	0	120										
S20	0	>1000	**	**										
min	0	14	0	2	min	0	0	0	0	min	0	0	1	2
max	1000	1000	65	850	max	17	1000	76	1280	max	0	15	2	224
mean	60	408	6	108	mean	1	276	5	166	mean	0	8	2	93
STD	220	363	15	186	STD	5	343	19	315	STD	0	8	0	95

** = Sample not measured due unavailability of borehole water

Table 4.13. F-Test statistics for total coliform and *E.coli* in dry and wet season for variances

	Household				**School Samples**			
Variable	**Total Coliform**		***E. coli***		**Total Coliform**		***E. coli***	
Season	*Wet*	*Dry*	*Dry*	*Wet*	*Dry*	*Wet*	*Wet*	*Dry*
Mean	352.77	150.86	5.43	1.31	423.97	114.12	62.63	5,82
Variance	158444.86	110789.52	412.57	22.23	141064.07	38150.49	53420.47	252,40
Observations	13.00	14.00	14.00	13.00	19.00	17.00	19.00	17,00
df	12.00	13.00	13.00	12.00	18.00	16.00	18.00	16,00
F	1.43		18.56		3.70		211.65	
P(F<=f) one-tail	0.27		5.95E-06		5.74E-03		1.17E-15	
F Critical one-tail	2.6		2.66		2.30		2.3	

A very strong positive significant correlation between EC with TDS, TH, HCO_3^- (r= 0.99, 1.00, 0.89, respectively) was observed in dry season while, EC had a moderate correlation with TDS and TH (r= 0.59 and 0.57, respectively) in wet season. TDS had a very strong positive correlation with TH (r= 0.99) in dry season while, it reduces to moderate positive (r=0.58) in wet season.

The correlation among TDS with TH (p value of 1.82E-12) was statistically significant only in dry season. Furthermore, EC had a strong significant positive correlation with salinity (r= 1.00 and 0.71 with p-value of 7.55E-58 and 0.02) and chlorine ion (r= 0.99 and 0.89 with p-value of 3.28E-12 and 4.21E-04) in dry and wet season respectively. pH had a negative insignificant correlation (r= -0.4-0.0) with all parameters throughout the assessment apart from fluoride ion and temperature in dry season which is comparable with the outcomes of the study by Heydarirad et al. (2019), .

Generally, total hardness had a positive Pearson correlation (at range between 0.44-1.00 and 0.44-1.0) with 62.5% (number of parameters= 16) of parameters in this study in dry and wet season respectively, in household samples while, a positive correlation among total hardness with 62.5% of parameters were observed in school samples at range between 0.51-0.95 and 0.45-0.95 in dry and wet season, respectively. This suggest that Mg and Ca were the major contributor to groundwater quality of Collins Chabane and Makhado Municipality as total hardness is derived from access concentration of Ca, Mg and Fe (Sawyer and McCarty 1967). This suggestion is further supported by the occurrence of significant correlations between TH with Mg and Ca which is strongly positive throughout the assessment in this study as shown in table 4.14 and 4.15.

Table 4.14 . Pearson correlation matrix of physicochemical parameters among groundwater samples from schools of Collins Chabane and Makhado municipality**.**

Dry	**pH**	**EC**	**TDS**	**Temp**	**Salinity**	**Cl^-**	**NO_3^-**	**F^-**	**SO_4^{-2}**	**PO_4^{-3}**	**HCO_3^-**	**Ca**	**Mg**	**K**	**Na**	**TH**	**Wet season**
pH	1.00	0.455*	0.455*	-0.16	0.30	-0.01	0.05	0.34	-0.22	0.29	0.35	0.35	0.44	0.02	0.28	**0.451***	pH
EC	0.22	1.00	1.000**	-0.621**	0.914**	0.604**	0.533*	0.732**	0.38	0.04	0.730**	0.802**	0.863**	0.11	0.604**	0.935**	EC
TDS	0.450*	0.805**	1.00	-0.621**	0.914**	0.604**	0.533*	0.732**	0.38	0.04	0.730**	0.802**	0.863**	0.11	0.604**	0.935**	TDS
Temp	0.06	0.20	0.23	1.00	-0.657**	-0.41	-0.44	-0.45	-0.518*	-0.14	-0.37	-0.523*	-0.512*	-0.15	-0.32	-0.556*	Temp
Salinity	0.36	0.848**	0.796**	0.16	1.00	0.632**	0.529*	0.667**	0.35	0.16	0.691**	0.809**	0.759**	0.16	0.555*	0.863**	Salinity
Cl^-	-0.07	0.691**	0.40	0.31	0.584**	1.00	0.808**	0.23	0.684**	-0.08	0.21	0.538*	0.37	0.07	0.519*	0.474*	Cl-
NO_3^-	-0.12	0.700**	0.43	0.41	0.620**	0.869**	1.00	0.07	0.787**	-0.17	0.15	0.39	0.41	0.28	0.20	0.448*	NO3-
F^-	0.674**	0.557*	0.515*	0.06	0.531*	0.24	0.19	1.00	-0.05	0.01	0.837**	0.710**	0.505*	0.05	0.687**	0.642**	F-
SO_4^{-2}	-0.35	0.614**	0.21	0.39	0.34	0.714**	0.772**	0.00	1.00	-0.04	-0.10	0.27	0.27	0.27	0.06	0.30	SO4-2
PO_4^{-3}	0.39	0.26	0.21	-0.20	0.26	0.18	0.03	0.737**	-0.24	1.00	-0.08	0.41	0.01	-0.02	-0.05	0.17	PO4-3
HCO_3^-	0.614**	0.561*	0.592**	0.00	0.701**	0.17	0.19	0.814**	-0.02	0.40	1.00	0.650**	0.624**	-0.16	0.545*	0.704**	HCO3-
Ca	0.485*	0.535*	0.32	0.03	0.634**	0.537*	0.482*	0.695**	0.31	0.36	0.724**	1.00	0.583**	-0.05	0.514*	0.812**	Ca
Mg	0.464*	0.725**	0.726**	0.19	0.793**	0.40	0.500*	0.545*	0.28	0.10	0.725**	0.674**	1.00	0.14	0.21	0.948**	Mg
K	-0.26	0.35	0.35	-0.03	0.26	0.18	0.40	0.02	0.41	-0.23	0.26	0.04	0.37	1.00	-0.14	0.08	K
Na	0.561*	0.598**	0.470*	-0.01	0.538*	0.490*	0.29	0.744**	0.10	0.756**	0.502*	0.530*	0.26	-0.18	1.00	0.35	Na
TH	**0.514***	0.707**	0.613**	0.14	0.794**	0.496*	0.537*	0.658**	0.32	0.22	0.789**	0.875**	0.948**	0.26	0.40	1.00	TH

*Correlation is significant at the 0.05 level (2-tailed). **Correlation is significant at the 0.01 level ☐ Dry season ▨ Wet

Table 4.15 . Pearson correlation matrix of physicochemical parameters among groundwater samples from household of Collins Chabane and Makhado municipality**.**

Dry	**pH**	**EC**	**TDS**	**Temp**	**Salinity**	**Cl^-**	**NO_3^-**	**F^-**	**SO_4^{-2}**	**PO_4^{-3}**	**HCO_3^-**	**Ca**	**Mg**	**K**	**Na**	**TH**	**Wet season**
pH	1.00	-0.51	-0.29	-0.46	-0.47	-0.53	-0.51	-0.29	-0.48	-0.28	-0.14	-0.46	-0.44	-0.31	-0.37	-0.49	pH
EC	-0.32	1.00	0.59	0.50	0.708*	0.875**	0.753**	0.50	0.713*	0.30	0.02	0.611*	0.46	0.48	0.709*	0.57	EC
TDS	-0.38	0.990**	1.00	-0.28	0.57	0.580*	0.37	0.14	0.43	-0.26	-0.01	0.586*	0.48	0.13	0.50	0.58	TDS
Temp	0.15	0.39	0.34	1.00	0.46	0.21	0.24	0.54	0.13	0.35	0.33	0.26	0.22	0.29	0.21	0.23	Temp
Salinity	-0.32	1.000**	0.990**	0.39	1.00	-0.04	0.06	0.13	0.41	0.39	-0.13	-0.01	-0.01	0.589*	0.38	-0.01	Salinity
Cl^-	-0.30	0.989**	0.984**	0.33	0.989**	1.00	0.983**	0.536*	0.50	-0.14	0.909**	0.989**	0.982**	0.17	0.48	0.989**	Cl^-
NO_3^-	-0.24	0.39	0.39	0.17	0.39	0.40	1.00	0.52	0.545*	-0.01	0.880**	0.963**	0.977**	0.34	0.51	0.975**	NO_3^-
F^-	0.07	0.647**	0.609*	0.648**	0.647**	0.604*	-0.04	1.00	0.22	-0.21	0.711**	0.622*	0.591*	0.02	0.53	0.606*	F^-
SO_4^{-2}	-0.45	0.48	0.50	0.03	0.48	0.48	0.679**	0.08	1.00	-0.03	0.28	0.46	0.42	0.19	0.805**	0.44	SO_4^{-2}
PO_4^{-3}	-0.12	-0.04	-0.02	0.03	-0.04	-0.02	0.894**	-0.30	0.51	1.00	-0.14	-0.17	-0.08	0.719**	-0.29	-0.12	PO_4^{-3}
HCO_3^-	-0.26	0.887**	0.842**	0.48	0.887**	0.860**	0.17	0.600*	0.21	-0.25	1.00	0.930**	0.936**	0.12	0.34	0.937**	HCO_3^-
Ca	-0.26	0.989**	0.974**	0.38	0.989**	0.989**	0.37	0.678**	0.42	-0.05	0.871**	1.00	0.983**	0.13	0.49	0.994**	Ca
Mg	-0.34	0.997**	0.985**	0.38	0.997**	0.987**	0.40	0.622*	0.45	-0.03	0.896**	0.986**	1.00	0.25	0.43	0.997**	Mg
K	-0.11	0.32	0.32	0.28	0.32	0.26	0.30	0.06	0.20	0.11	0.46	0.22	0.34	1.00	0.07	0.20	K
Na	-0.47	0.748**	0.764**	0.10	0.748**	0.748**	0.22	0.47	0.753**	-0.10	0.530*	0.717**	0.715**	0.05	1.00	0.46	Na
TH	-0.31	0.997**	0.984**	0.38	0.997**	0.991**	0.39	0.647**	0.44	-0.04	0.889**	0.995**	0.998**	0.29	0.718**	1.00	TH

*Correlation is significant at the 0.05 level (2-tailed). **Correlation is significant at the 0.01 level (2-tailed). ☐ Dry season ▨ Wet

4.7.2 Correlation matrix among major cation and anions in groundwater samples

A strong positive significant correlation of NO_3^- with Cl^- (r=0.869 and 0.808, P=1.41E-06 and 1.65E-05) and SO_4^{-2} (r=0.772 and 0.787, P=1.08E-04 and 3.87E-05) were observed during dry and wet season, respectively in school samples. Meanwhile Cl correlated positively with Na (r= 0.490, 0.519; P=0.03, 0.02, respectively at 0.05 significant level) during dry and wet season, respectively.

The positive relationship between NO_3^- with Cl^- and Na with Cl^- suggest that these parameters could be possibly originating from the anthropogenic sources such as same manure from agricultural activities and waste from pit toilets (Kohn et al., 2016). Similarly, Odiyo et al. (2020) also reported a positive correlation between NO_3^- with Cl^- in groundwater samples collected from schools in Vhuronga 1, Limpopo province (RSA) which support the findings of this study.

The study area of this study consists of schools which use both flashing toilet and pit latrines for sanitation and have small gardens which are potential sources of faecal contamination. This suggests that a positive correlation between NO_3^- with Cl^- in school samples is associated with agricultural activities and faecal contamination from pit latrines and septic storages.

Correlation analysis (Table 4.14) showed a moderate positive significant correlation of F^- with calcium, magnesium (Mg), sodium and total hardness (TH) from dry season to wet season, with Pearson correlation values in the range between 0.505 to 0.744 at 0.01 significant level throughout the assessment. These elements (calcium, sodium and total hardness) correlate significantly at 0.01 level apart from magnesium which had p-values (0.02 and 0.023) which are less than α (0.05) in dry and wet season. TH had a moderate positive correlation with NO_3^- and Cl^- (r = 0.537- 0.448 and 0.496- 0.474, respectively) at 0.01 significant level, while strong positive correlation was observed with HCO_3^- (r= 0.789-0.704, P=6.01E-05-5.29E-04) and Ca (r= 0.875-0.812, P= 9.63E-07-1.39E-05) during dry and wet season, respectively. A very strong positive correlation (r= 0.948) was observed between TH and Mg (P = 7.58E-10 and 2.31E-10) at 99% significant level during dry and wet season, respectively. The correlations were statistically significant since p-values were less than α (0.01).

In household samples, a very strong relationship among ions and cations were also observed, Cl^- exhibited relationship with Ca (r= 0.989 and 0.989), Na (r) Mg (r= 0.982 and 0.987) and TH (r= 0.989 and 0.991) in dry and wet season, respectively while, Cl correlated positively with Na (r= 0.748, 0.481; P= 0.001, 0.082), respectively) during dry and wet season, respectively. Similarly, previous studies such as Saha et al. (2019) and Odiyo et al. (2020) reported a moderate positive correlation between Na and Cl in groundwater samples from Rangpur (Bangladesh) and Vhuronga 1 region of Limpopo province (South Africa), respectively. The positive relationship between these parameters could be possibly originating from the natural source such as dissolution of Halite and anthropogenic sources such as agricultural activities and waste from pit toilets (Kumar and James, 2016; Saha et a., 2019; Li, et al., 2021).

NO_3^- showed a very strong and strong positive significant correlation with Ca (r= 0.963), Mg (r= 0.977), TH (r= 0.975) and HCO_3^-, (r= 0.880) in wet season while in dry season, it significantly correlated positive with SO_4^- (r=0.679, P=0.005) and PO_4^{3-}(r=0.894, P= 6.81E-06) only. These findings evident that their distributions could be from the same possible sources or preferably controlled by the same factor. A weak positive correlation was observed between K and PO_4^{3-}(r= 0.340, P=0.215) in dry season which was statistically not significant meanwhile in wet season, a strong positive correlation (r= 0.719) was observed at 0.01 significant level with P-value of 0.004.

Correlation analysis for communal samples were performed for dry season only due to low quantity of sample in wet season. Communal samples (C1-C3) show a very strong positive correlation between TH - NO_3^-(r= 0.999), F^- - Na (r=0.998), and K - Mg (r= 0.998) with P-value of 0.035, 0.040 and 0.036, respectively (Table 4.16). These pairs were statistically significant since P-values were less than α (0.05). Similar study by Zainol et al. (2021) found similar positive correlation value between K and Mg ($r = 0.981$, $p < 0.01$) which suggest for possible leaching of salts from secondary salts. The correlation results further showed a stronger negative correlation of PO_4^{3-} with TH (r= -0.771, P= 0.439), Na (r= -0.714, P= 0.494), NO_3^-(r= -0.736, P=0.474), Cl^-(r= -0.992, P= 0.083 and SO_4^{2-} (r= -0.976, P= 0.139) which were not statistically significant, since p-values were greater than α (0.05). HCO_3^- exhibited a very strong negative correlation with Mg (r= -0.993, P= 0.077) and K (r= -0.984, P= 0.114), while strong negative and positive correlation of HCO_3^- were also observed with TH (r= -0.746, P= 0.463) and Ca (r= 0.832, P= 0.374) which further support the co-existence of these parameters from bicarbonate rock as revealed by Gibbs diagram (Fig. 4.15 and 16).

Table 4.16 Pearson correlation matrix of chemical parameters among groundwater samples from communal boreholes of Collins Chabane and Makhado municipality.

	Cl^-	**NO_3^-**	**F^-**	**SO_4^{-2}**	**PO_4^{-3}**	**HCO_3^-**	**Ca**	**Mg**	**K**	**Na**	**TH**
Cl^-	1.00	0.64	0.76	0.94	-0.99	-0.02	0.53	0.14	0.20	0.80	0.68
		0.56	0.45	0.22	0.08	0.99	0.64	0.91	0.87	0.41	0.52
NO_3^-	0.64	1.00	-0.01	0.87	-0.74	-0.78	-0.30	0.85	0.88	0.05	**0.999***
	0.56		0.99	0.33	0.47	0.43	0.80	0.35	0.32	0.97	0.03
F^-	0.76	-0.01	1.00	0.49	-0.67	0.63	0.96	-0.53	-0.48	**0.998***	0.04
	0.45	0.99		0.67	0.53	0.56	0.19	0.64	0.68	0.04	0.97
SO_4^{-2}	0.94	0.87	0.49	1.00	-0.98	-0.36	0.21	0.47	0.52	0.55	0.89
	0.22	0.33	0.67		0.14	0.76	0.86	0.69	0.65	0.63	0.30
PO_4^{-3}	-0.99	-0.74	-0.67	-0.98	1.00	0.15	-0.42	-0.27	-0.33	-0.71	-0.77
	0.08	0.47	0.53	0.14		0.90	0.72	0.83	0.79	0.49	0.44
HCO_3^-	-0.02	-0.78	0.63	-0.36	0.15	1.00	0.83	-0.99	-0.98	0.58	-0.75
	0.99	0.43	0.56	0.76	0.90		0.37	0.08	0.11	0.60	0.46
Ca	0.53	-0.30	0.96	0.21	-0.42	0.83	1.00	-0.76	-0.72	0.94	-0.25
	0.64	0.80	0.19	0.86	0.72	0.37		0.45	0.49	0.23	0.84
Mg	0.14	0.85	-0.53	0.47	-0.27	-0.99	-0.76	1.00	**0.998***	-0.48	0.82
	0.91	0.35	0.64	0.69	0.83	0.08	0.45		0.04	0.68	0.39
K	0.20	0.88	-0.48	0.52	-0.33	-0.98	-0.72	**0.998***	1.00	-0.43	0.85
	0.87	0.32	0.68	0.65	0.79	0.11	0.49	0.04		0.72	0.35
Na	0.80	0.05	**0.998***	0.55	-0.71	0.58	0.94	-0.48	-0.43	1.00	0.11
	0.41	0.97	0.04	0.63	0.49	0.60	0.23	0.68	0.72		0.93
TH	0.68	**0.999***	0.04	0.89	-0.77	-0.75	-0.25	0.82	0.85	0.11	1.00
	0.52	0.03	0.97	0.30	0.44	0.46	0.84	0.39	0.35	0.93	

*. Correlation is significant at the 0.05 level (2-tailed).

4.7.3 Pearson correlation matrix among trace metals in the groundwater samples

A moderate negative significant correlation of Hg with Cr (r= -0.662, p= 0.001) and Mn (r= -0.546, P= 0.013) were observed during wet season in school samples. While Hg and Mn (r= 0.492, P= 0.032) had a moderate correlation at 0.05 significant level in dry period. Pb exhibited a relationship with Zn and Cu (r= 0.532-0.504, 0.532-0.904, P=0.019 -0.024, 0.019-4.68E-08, respectively), while Cu correlated with Zn (r= 0.325-0.558, P= 0.175 -0.011) throughout the assessment while, Hg correlated negatively with Cr (r= -0.662, P=0.001) in wet season Zn with Pb (r= 0.532-0.504, P=0.019 -0.024) during dry and wet period Cu with Zn (r= 0.325-0.558, P= 0.175 -0.011 and Pb (r= 0.532-0.904, P=0.019-4.68E-08) throughout the study period (Table 4.17).

Boateng et al. (2019) reported similar results of a moderate negative and positive correlation of Pb with Zn and Cu (r= − 0.477, 0.430, respectively). Positive correlation and negative correlation of Pb with Zn/Cu and Hg with Cr suggests that both metals are influenced by common and different anthropogenic activities, respectively (Boateng et al., 2019). Table 4.18 shows inter relationship among trace metals in the borehole water samples collected from households. The results show a very strong significant correlation between Fe and Al (r= 0.995, P= 3.22E-14) in dry season. Meanwhile Pb and Cr (r=0.794, P=0.006) and Ni (r= 0.529, P= 0.116) had a strong and moderate positive correlation in wet season. Fe correlated very strongly with Al, which suggests that they co-exist from same source. Fe and Al could be leached from the same geogenic sources as they are common elements found in minerals and rocks (Zainol et al., 2021). Pb had a weak and strong positive correlation with Cu (0.333-0.354, P= 0.225-0.315) and Mn (r= 0.818-855, P= 1.97E-04-0.002) throughout the season, respectively. Correlation between Cu and Pb was not statistically significant while, Cu an Mn had a significant correlation since p-values was less than α (0.01). unfortunately, due to low number of sample correlation for communal samples was certainly not meaningful.

The source of ions and trace metals such as Cl, NO_3^-, Pb, Fe, Ni, and Cr concentration in groundwater could be dissolution from natural sources and atmospheric deposition, application of fertilizers, herbicide, pesticides and organic manure (from livestock waste) from household and school farmlands, use of detergent and linkages of waste from household and school plumbing and septic tanks or pit toilets (Mahmood et al. 1998; Jose et al., 2014; Zhou, 2015; Pazand et al., 2018; Rezaei et ai., 2019; Odiyo et al., 2020).

Table 4.17 Correlation matrix among trace metals in the groundwater samples collected from schools

Dry season		V	Cr	Mn	Ni	Cu	Zn	Hg	Pb	Al	Fe	Wet season
V	Pearson Correlation	1	.559*	0.292	-0.101	0.068	0.141	-0.402	0.017	0.347	.594**	V
	Sig. (2-tailed)		0.010	0.211	0.673	0.776	0.553	0.079	0.945	0.134	0.006	
Cr	Pearson Correlation	0.054	1	0.444	0.198	0.244	0.237	**-.662****	0.200	0.046	.516*	Cr
	Sig. (2-tailed)	0.827		0.050	0.402	0.299	0.315	0.001	0.397	0.846	0.020	
Mn	Pearson Correlation	**.773****	-0.066	1	-0.122	-0.119	-0.069	**-.546***	-0.164	0.043	0.205	Mn
	Sig. (2-tailed)	1.03E-04	0.788		0.609	0.617	0.773	0.013	0.489	0.857	0.386	
Ni	Pearson Correlation	**-0.374**	-0.081	-0.166	1	.457*	**0.424**	0.062	0.175	.504*	-0.075	Ni
	Sig. (2-tailed)	0.115	0.743	0.496		0.043	0.063	0.794	0.460	0.024	0.752	
Cu	Pearson Correlation	-0.040	-0.215	-0.221	-0.103	1	**.558***	-0.257	.904**	0.286	-0.143	Cu
	Sig. (2-tailed)	0.871	0.377	0.364	0.676		0.011	0.273	4.68E-08	0.221	0.547	
Zn	Pearson Correlation	-0.108	-0.074	-0.212	**.654****	**0.325**	1	-0.333	**.504***	0.274	-0.270	Zn
	Sig. (2-tailed)	0.660	0.763	0.384	0.002	0.175		0.151	0.024	0.243	0.249	
Hg	Pearson Correlation	0.324	-0.083	**.492***	-0.282	-0.079	-0.320	1	-0.354	0.080	-0.199	Hg
	Sig. (2-tailed)	0.175	0.736	0.032	0.242	0.748	0.181		0.126	0.738	0.400	
Pb	Pearson Correlation	-0.139	-0.257	-0.204	-0.027	**.532***	**0.424821**	0.071	1.000	0.106	-0.187	Pb
	Sig. (2-tailed)	0.571	0.289	0.403	0.914	0.019	0.070	0.771		0.656	0.430	
Al	Pearson Correlation	-0.336	-0.235	-0.225	0.059	-0.206	-0.250	0.089	-0.077	1	0.133	Al
	Sig. (2-tailed)	0.159	0.333	0.355	0.811	0.397	0.301	0.716	0.754		0.576	
Fe	Pearson Correlation	-0.226	0.064	-0.088	**0.393**	-0.225	-0.175	-0.060	-0.214	.479*	1	Fe
	Sig. (2-tailed)	0.352	0.793	0.722	0.096	0.354	0.474	0.806	0.379	0.038		

**. Correlation is significant at the 0.01 level (2-tailed).*. Correlation is significant at the 0.05 level (2-tailed).

▨ Wet season ☐ Dry season

Table 4.18. Correlation matrix among trace metals in the groundwater samples collected from household

Dry season		V	Cr	Mn	Ni	Cu	Zn	Hg	Pb	Al	Fe	Wet season
V	Pearson Correlation	1	0.387	0.440	-0.100	-0.215	-0.201	0.351	0.230	0.414	0.157	V
	Sig. (2-tailed)		0.269	0.203	0.783	0.551	0.578	0.320	0.523	0.234	0.666	
Cr	Pearson Correlation	0.335	1	0.873**	.697*	-0.042	-0.011	0.565	0.794**	0.589	-0.292	Cr
	Sig. (2-tailed)	0.222		0.001	0.025	0.909	0.975	0.089	0.006	0.073	0.413	
Mn	Pearson Correlation	0.311	0.288	1	0.442	-0.014	0.089	0.775**	**0.855****	0.463	-0.176	Mn
	Sig. (2-tailed)	0.260	0.297		0.201	0.969	0.808	0.009	0.002	0.178	0.626	
Ni	Pearson Correlation	-0.077	0.243	**0.570***	1	0.178	0.210	0.107	**0.529**	0.502	-0.378	Ni
	Sig. (2-tailed)	0.784	0.382	0.026		0.623	0.560	0.768	0.116	0.139	0.281	
Cu	Pearson Correlation	0.054	-0.417	0.353	0.143	1	0.370	-0.067	0.354	0.244	0.508	Cu
	Sig. (2-tailed)	0.847	0.122	0.197	0.611		0.292	0.853	0.315	0.498	0.134	
Zn	Pearson Correlation	0.078	-0.005	.598*	**0.714****	.608*	1	-0.235	0.241	0.262	-0.002	Zn
	Sig. (2-tailed)	0.783	0.987	0.019	0.003	0.016		0.513	0.502	0.465	0.995	
Hg	Pearson Correlation	-0.094	-0.248	0.117	0.117	0.286	0.126	1	0.524	0.002	-0.251	Hg
	Sig. (2-tailed)	0.740	0.373	0.677	0.678	0.301	0.656		0.120	0.996	0.485	
Pb	Pearson Correlation	0.500	0.378	**0.818****	0.366	0.333	**0.515***	-0.171	1	0.417	0.063	Pb
	Sig. (2-tailed)	0.058	0.165	1.97E-04	0.180	0.225	0.050	0.542		0.230	0.862	
Al	Pearson Correlation	0.426	0.024	-0.268	-0.163	-0.135	-0.266	-0.191	-0.152	1	-0.017	Al
	Sig. (2-tailed)	0.113	0.931	0.334	0.562	0.631	0.339	0.495	0.590		0.953	
Fe	Pearson Correlation	0.403	-0.006	-0.274	-0.132	-0.068	-0.202	-0.145	-0.163	**.995****	1	Fe
	Sig. (2-tailed)	0.136	0.982	0.323	0.638	0.809	0.469	0.607	0.562	3.22E-14		

*. Correlation is significant at the 0.05 level (2-tailed).**. Correlation is significant at the 0.01 level (2-tailed).

▨ Wet season ☐ Dry season

4.8 Conclusions on the evaluation of microbial and physicochemical contaminants associated with groundwater from Collins Chabane and Makhado municipality

From the results obtained, the pH values were above the neutral value of 7.0, they were still within the recommended SANS 241 (2015) guidelines value of 5.0 to 9.7 for domestic water use except from pH level of 10.83 which was obtained from household sample (P4) during wet season (November 2019).

The EC and TDS values for all collected samples within selected primary schools, individual household and communal boreholes were within the recommended limits set by SANS 241 of <1700 µS/cm and <1200 mg/L for EC and TDS during both dry and wet season (November) apart from sample P12. The results indicate that 14.29% and 35.29% of groundwater in school and household were slightly salty (>1000 µS/cm) in dry season (October, 2019). EC exhibited a positive significant correlation at 0.01 significant level with TDS, TH and salinity in the entire groundwater samples.

Turbidity from all boreholes were within the standard limits of 1 NTU by WHO (2017) and SANS (2015). About 30% schools of borehole water samples were above the standard limits concentration of total NO_3^- concentration of 50 mg/L set by WHO (2015). Meanwhile, 41.03, 58.82, and 40% of sample collected from schools, private household and communal borehole also exceeded the acceptable limits respectively, throughout the entire study period.

All borehole water sample were found with no human health concern with regard to excess concentration of fluoride apart from school borehole (S1) and household borehole (P12). Since there is no evidence of anthropogenic sources of fluoride contamination, this study suggests that weathering and leaching of fluoride-bearing minerals from rocks and sediments could be the possible source of F^- contamination in those boreholes.

Major ions concentration in borehole samples such as Mg, Ca, Na, K and B were assessed to achieve the objective of this study. The detected concentrations of Na, K and B ions were within the desired standard limits of SANS 241 (2015). However, excessive amount of Mg concentration was found in 20% and 60% of school and household borehole, respectively during the study period. Furthermore, high concentration levels of Ca were found in 41.02%, 68.97% and 40% of school, household and communal borehole respectively, during the entire study period.

In order to understand water quality based on trace metals, the concentration of trace metals such as As, Sb, Cd, Bi, Co, Hg, Pb, U, Zn, Mn, V and Cu were assessed. The concentrations these elements across all samples complied with SANS 241 and WHO standard guideline. Furthermore, Al (5.13, 3.57, and 0.00%), Cr (15.39, 4.00 and 20.00%), and Ni concentration (2.56, 0.00 and 0.00%) in water samples (school, household and communal samples respectively) were detected at above the permissible limit set by SANS 241 and WHO. High concentrations of Al, Cr and Mg gradually increased during the wet season meanwhile nickel concentration decreased.

According to Gibbs diagram analysis, most groundwater samples assembled in the weathering and rock dominance region. According to piper plot, the groundwater water was dominated by Mg, HCO_3^- and Cl ions which makes the groundwater type Ca-Mg-HCO_3^- and Mg-Cl water type. None of samples had hardness of <60 mg/L, 1.32% had hardness between 60 and 120 mg/L, 6.85% had hardness between 120 and 180 mg/L, and 91.83% (n= 73) had hardness of >180 mg/L. This denotes that the water is hard in nature and originate from/within carbonic rock and magnesite mineral. Generally, samples collected from primary school and private communal boreholes were dominated by Mg-HCO_3^- and Mg-Cl water type, respectively. In general, Ca^{2+} have a very strong positive correlation with Mg^{2+} and HCO_3^- in borehole water samples which further suggest the co-existence of these parameters from bicarbonate rock as supported by Gibbs diagram.

A major risk to the health of school learners is microbial contamination of groundwater. 100% of samples collected from school (S1-S20) boreholes in dry season failed to comply with SANS guideline. While 50% of groundwater samples had no counts of *E. coli*. The results further indicate that groundwater from only 5.56% borehole sites (household and communal) had no counts of *E. coli*. There was a statistical difference between the means of total coliform and *E.coli* in groundwater samples except for total coliform means of household water samples in dry and wet season with p-value of 0.27. Based on WQI analysis, borehole water quality of Collins Chabane and Makhado municipality fell under four category class, which is excellent, good, poor and unsuitable. All school samples and communal samples fell under excellent and good category except for sample S1 and S2 which fell under poor category in dry and wet season, respectively. while, excellent (21.43%), good (46.43%), poor (21.43%), and unsuitable (10.71%) were obtained from household sample during the assessment.

CHAPTER FIVE: POTENTIAL HUMAN HEALTH RISKS OF HEAVY METALS AND MICROBIAL CONCENTRATION IN THE INVESTIGATED GROUNDWATER IN COLLINS CHABANE AND MAKHADO MUNICIPALITY

5.1 Introduction

This chapter is aimed at evaluating the occurrence and potential health risk associated with the sampled groundwater from the study area. This section covers health risk assessment which has been achieved through computation of risk assessment which include hazard identification, exposure assessment, dose-response (toxicity) and risk characterization (Adamu et al., 2015).The health risk assessment of each potentially toxic heavy metals were based on the quantification of the risk level and expressed in terms of cancer and non-cancer health risks (Sun et al., 2015).

5.2 **Potential Human Health Risk Assessment**

Health risk assessment model were assessed through evaluation of the health risks that trace metal could pose on children and adult via direct ingestion (D_{ing}) and dermal absorption (D_{derm}) routes of groundwater consumption. The level of exposure (EXPs) through D_{ing} and D_{derm} were assessed for the dry (October 2019) and wet season (November 2019). For this study's purpose, the health-related risk associated with ingestion exposure was determined using the minimum and maximum values of Zn, Mn, Ni, Cu, Cd, As, Cr, Pb, Co, Hg, and Fe concentration obtained from the investigated boreholes. Table 5.1 to Table 5.4 show the variation of the EXPs, Chronic risk assessment (CDIs), and Hazard quotient (HQs) of the selected heavy metals for both children and adults during the study.

The maximum values of D_{ing} ranged between 4.40E-06-9.50E+00 and 2.80E-04-2.50E+00 for children and adult for schools during the dry season (Table 5.1) while 8.20E-06-3.70E+01 and 3.10E-04-9.70E+00 for the wet season (Table 5.2), respectively. As in shown in Appendix Table 5.1, the high average values of Mn (5.3E+00), Cr (4.4E+00), Zn (3.3E+00) and Ni (2.6E+00) are the major contributors of health exposure through ingestion pathway for children, meanwhile Cr and Mn had high average values of 1.2E+00 and 1.4E+00 for adult in dry season. During wet season Cr, Ni and Zn had the high average values of 5.17E+00, 4.83E+00 and 3.35E+00 for children respectively whilst adult had Cr (1.35E+00)and Ni (1.26E+00) being the major of health exposure through ingestion pathway (Appendix 8: Table 5.11).

The level of health exposure (EXPs) through dermal absorption (D_{derm}) pathway were also estimated for both children and adult in groundwater samples. The maximum values of D_{derm} ranged between 3.90E-06-1.10E+00 and 1.20E-10-6.30E-01 for children and adult for schools during dry season (Table 5.1) while 4.40E-06-7.30E-01 and 2.10E-09-4.30E-01for wet season (Table 5.2), respectively. There is no high risk of non-carcinogenic health risk via dermal pathway exposure to both children and adult wexcept for Hg (1.10E+00) in dry season.

5.2.1 Health related risk associated with ingestion and dermal exposure pathway of groundwater from selected household with communal sites

The maximum values of ingestion exposure (D_{ing}) ranged between 8.10E-06-3.70E+01 and 4.60E-04-9.70E+00 for children and adult for communal and household during dry season (Table 5.3) while 1.10E-05-1.30E+01 and 3.10E-04-3.50E+00 for wet season (Table 5.4), respectively.

As compared to the considered parameters in this study, Higher estimated D_{ing} recorded average values of Zn, Ni and Cr for children (4.9E+00, 4.8E+00 and 3.9E+00) and adult (1.3E+00, 1.3E+00 and 1.0E+00) were observed in the dry season; meanwhile 4.76E+00, 2.80E+00 and 4.78E+00 for children and 1.25E+00, 7.33E-01 and 1.25E+00 for adult were observed in wet season, respectively (Appendix Table 5.3). Furthermore, high average value for Cu (1.18E+00) was computed for children in the wet season. The concentration of heavy metals can increase due to groundwater interacting with surface water due to high infiltration of rainwater in wet season which can carry Cu particles among other metals from automobiles (Małecki et al., 2017; Edokpayi et al., 2018c).

Furthermore, while Zn, Ni and Cr are the main drivers of risk of non-carcinogenic health conditions, their average values in the dry season are slightly higher than in the wet season, which indicate that higher possible health risk in consumption of household and communal can occur mostly in the dry season. These findings contradict with the findings of Durowoju et al. (2020).

The maximum values of D_{derm} ranged between 6.40E-06-9.50E-01 and 2.00E-10-5.60E-01 for children and adult for communal and household during dry season (Table 5.3) while 4.40E-06-2.40E+00 and 2.10E-09-1.40E+00 for wet season (Table 5.4), respectively. The is negligible risk of non-carcinogenic occurrence via dermal pathway exposure to both children and adult with exclusion of Hg in wet season to both children (2.40E+00) and adult (1.40E+00) in groundwater from communal and household (Table 5.4).

Table 5.1: The Maximum and minimum values for selected heavy metals of human health risk assessment for dry season in primary schools

Heavy Metal	**R*f*Ding (µg/kg/day)**	**R*f*Dderm (µg/kg/day)**	**Stats.Parameter**	**Ding (Child)**	**Ding (Adult)**	**HQing (Child)**	**HQing (Adult)**	**CRing (child)**	**CRing (Adult)**	**CDIing (Child)**	**CDIing (Adult)**	**Dderm (Child)**	**Dderm (Adult)**	**HQderm (Child)**	**HQderm (Adult)**
As	3.0E-01		Min	3.6E-01	9.4E-02	2.7E+02	1.2E+02	2.4E-04	6.3E-05	3.6E-01	9.4E-02	1.3E-03	7.7E-04	2.0E+02	3.5E+02
			Max	4.1E-01	1.1E-01	2.7E+02	1.2E+02	2.7E-04	7.1E-05	4.1E-01	1.1E-01	1.5E-03	8.7E-04	2.3E+02	3.9E+02
Fe	7.0E+02	1.4E+02	Min	4.4E-06	2.8E-04	1.2E-01	2.3E+06	ND	ND	1.1E-03	2.8E-04	3.9E-06	1.2E-10	1.9E+07	6.2E+11
			Max	4.4E-06	2.6E-03	1.2E-01	2.3E+06	ND	ND	9.9E-03	2.6E-03	3.6E-05	1.1E-09	1.8E+08	5.9E+12
Cr	3.0E+00		Min	3.7E+00	9.8E-01	1.4E+02	6.1E+01	7.5E-03	1.3E-02	3.7E+00	9.8E-01	2.7E-02	1.6E-02	6.4E+01	1.1E+02
			Max	6.4E+00	1.7E+00	1.4E+02	6.1E+01	2.0E-03	3.4E-03	6.4E+00	1.7E+00	4.7E-02	2.7E-02	1.1E+02	1.9E+02
Mn	2.4E+01		Min	3.0E+00	7.8E-01	2.7E+02	1.2E+02	ND	ND	3.0E+00	7.8E-01	1.1E-02	6.4E-03	6.9E+02	1.2E+03
			Max	9.5E+00	2.5E+00	2.7E+02	1.2E+02	ND	ND	9.5E+00	2.5E+00	3.5E-02	2.0E-02	2.2E+03	3.7E+03
Co	2.0E+01		Min	3.6E-02	9.3E-03	2.7E+01	1.2E+01	ND	ND	3.6E-02	9.3E-03	1.3E-03	7.6E-04	6.3E+03	1.1E+04
			Max	8.6E-02	2.3E-02	2.7E+01	1.2E+01	ND	ND	8.6E-02	2.3E-02	3.2E-03	1.8E-03	1.5E+04	2.6E+04
Ni	2.0E+01		Min	2.1E+00	5.5E-01	2.7E+02	1.2E+02	ND	ND	2.1E+00	5.5E-01	7.8E-03	4.5E-03	4.9E+04	8.3E+04
			Max	3.9E+00	1.0E+00	2.7E+02	1.2E+02	ND	ND	3.9E+00	1.0E+00	1.4E-02	8.4E-03	4.9E+04	1.5E+05
Cu	4.0E+01		Min	1.2E-01	3.2E-02	2.7E+02	1.2E+02	ND	ND	1.2E-01	3.2E-02	4.5E-04	2.6E-04	1.5E+04	2.6E+04
			Max	7.2E-01	1.9E-01	2.7E+02	1.2E+02	ND	ND	7.2E-01	1.9E-01	2.7E-03	1.6E-03	1.5E+04	1.5E+05
Zn	3.0E+01		Min	1.9E+00	4.9E-01	4.5E+02	2.0E+02	ND	ND	1.9E+00	4.9E-01	4.1E-03	2.4E-03	1.6E+03	2.8E+03
			Max	8.3E+00	2.2E+00	4.5E+02	2.0E+02	ND	ND	8.3E+00	2.2E+00	1.8E-02	1.1E-02	1.6E+03	1.2E+04
Cd	1.0E+00		Min	3.6E-03	9.4E-04	2.7E+02	1.2E+02	5.7E-07	1.5E-07	3.6E-03	9.4E-04	1.3E-05	7.7E-06	1.3E+04	2.2E+04
			Max	1.1E-02	2.8E-03	2.7E+02	1.2E+02	1.7E-06	4.5E-07	1.1E-02	2.8E-03	4.0E-05	2.3E-05	1.3E+04	6.5E+04
Hg	2.0E+02		Min	1.8E-01	4.6E-02	2.7E-01	1.2E-01	2.8E-05	7.3E-06	1.8E-01	4.6E-02	6.5E-01	3.8E-01	2.8E-01	4.7E-01
			Max	3.0E-01	7.7E-02	2.7E-01	1.2E-01	4.7E-05	1.2E-05	3.0E-01	7.7E-02	**1.1E+00**	6.3E-01	4.6E-01	7.9E-01
Pb	3.5E+00		Min	1.2E-02	3.0E-03	6.8E+01	3.1E+01	1.4E-03	3.6E-04	1.2E-02	3.0E-03	1.7E-04	1.0E-04	7.3E+02	1.3E+03
			Max	1.3E-01	3.4E-02	6.8E+01	3.1E+01	1.5E-02	4.0E-03	1.3E-01	3.4E-02	1.9E-03	1.1E-03	7.3E+02	1.4E+04

Table 5.2 The Maximum and minimum values for selected heavy metals of human health risk assessment for wet season in primary schools

	R*f*D$_{ing}$ (µg/kg/day)	R*f*D$_{derm}$ (µg/kg/day)	Stats. Parameter	D$_{ing}$ (Child)	D$_{ing}$ (Adult)	HQ$_{ing}$ (Child)	HQ$_{ing}$ (Adult)	CR$_{ing}$ (child)	CR$_{ing}$ (Adult)	CDI$_{ing}$ (Child)	CDI$_{ing}$ (Adult)	D$_{derm}$ (Child)	D$_{derm}$ (Adult)	HQ$_{derm}$ (Child)	HQ$_{derm}$ (Adult)
As	3.0E-01		Min	2.4E-01	6.3E-02	2.7E+02	1.2E+02	1.6E-04	4.2E-05	2.4E-01	6.3E-02	8.8E-04	5.1E-04	2.3E+02	3.9E+02
			Max	3.6E-01	9.4E-02	2.7E+02	1.2E+02	2.4E-04	6.3E-05	3.6E-01	9.4E-02	1.3E-03	7.7E-04	3.4E+02	5.8E+02
Fe	7.0E+02	1.4E+02	Min	8.2E-06	4.8E-03	1.2E-01	2.3E+06	ND	ND	1.8E-02	4.8E-03	6.7E-05	2.1E-09	1.0E+07	3.3E+11
			Max	8.2E-06	4.9E-03	1.2E-01	2.3E+06	ND	ND	1.9E-02	4.9E-03	6.8E-05	2.1E-09	1.0E+07	3.4E+11
Cr	3.0E+00		Min	3.9E+00	1.0E+00	1.4E+02	6.1E+01	7.7E-03	1.6E-02	3.9E+00	1.0E+00	2.8E-02	1.7E-02	5.0E+01	8.5E+01
			Max	8.2E+00	2.2E+00	1.4E+02	6.1E+01	2.0E-03	4.3E-03	8.2E+00	2.2E+00	6.0E-02	3.5E-02	1.1E+02	1.8E+02
Mn	2.4E+01		Min	2.6E-01	6.7E-02	2.7E+02	1.2E+02	ND	ND	2.6E-01	6.7E-02	9.4E-04	5.5E-04	2.1E+03	3.5E+03
			Max	3.2E+00	8.3E-01	2.7E+02	1.2E+02	ND	ND	3.2E+00	8.3E-01	1.2E-02	6.8E-03	2.5E+04	4.3E+04
Co	2.0E+01		Min	3.5E-02	9.2E-03	2.7E+01	1.2E+01	ND	ND	3.5E-02	9.2E-03	1.3E-03	7.5E-04	5.9E+03	1.0E+04
			Max	9.3E-02	2.4E-02	2.7E+01	1.2E+01	ND	ND	9.3E-02	2.4E-02	3.4E-03	2.0E-03	1.6E+04	2.7E+04
Ni	2.0E+01		Min	2.3E+00	6.0E-01	2.7E+02	1.2E+02	ND	ND	2.3E+00	6.0E-01	8.4E-03	4.9E-03	5.2E+03	8.8E+03
			Max	3.7E+01	9.7E+00	2.7E+02	1.2E+02	ND	ND	3.7E+01	9.7E+00	1.4E-01	7.9E-02	5.2E+03	1.4E+05
Cu	4.0E+01		Min	1.4E-01	3.6E-02	2.7E+02	1.2E+02	ND	ND	1.4E-01	3.6E-02	5.1E-04	3.0E-04	1.6E+03	2.7E+03
			Max	7.0E+00	1.8E+00	2.7E+02	1.2E+02	ND	ND	7.0E+00	1.8E+00	2.6E-02	1.5E-02	1.6E+03	1.3E+05
Zn	3.0E+01		Min	1.7E+00	4.6E-01	4.5E+02	2.0E+02	ND	ND	1.7E+00	4.6E-01	3.8E-03	2.2E-03	1.9E+03	3.3E+03
			Max	7.2E+00	1.9E+00	4.5E+02	2.0E+02	ND	ND	7.2E+00	1.9E+00	1.6E-02	9.2E-03	1.9E+03	1.3E+04
Cd	1.0E+00		Min	1.2E-03	3.1E-04	2.7E+02	1.2E+02	1.9E-07	5.0E-08	1.2E-03	3.1E-04	4.4E-06	2.6E-06	1.3E+04	2.2E+04
			Max	1.1E-02	2.8E-03	2.7E+02	1.2E+02	1.7E-06	4.5E-07	1.1E-02	2.8E-03	4.0E-05	2.3E-05	1.3E+04	1.9E+05
Hg	2.0E+02		Min	1.4E-01	3.6E-02	2.7E-01	1.2E-01	2.2E-05	5.7E-06	1.4E-01	3.6E-02	5.0E-01	2.9E-01	4.1E-01	7.0E-01
			Max	2.0E-01	5.2E-02	2.7E-01	1.2E-01	3.2E-05	8.3E-06	2.0E-01	5.2E-02	7.3E-01	4.3E-01	6.0E-01	1.0E+00
Pb	3.5E+00		Min	1.8E-02	4.8E-03	6.8E+01	3.1E+01	2.1E-03	5.6E-04	1.8E-02	4.8E-03	2.7E-04	1.6E-04	2.8E+02	4.7E+02
			Max	3.4E-01	9.0E-02	6.8E+01	3.1E+01	4.1E-02	1.1E-02	3.4E-01	9.0E-02	5.1E-03	3.0E-03	2.8E+02	9.0E+03

Table 5.3: The maximum and minimum values for selected heavy metals of human health risk assessment for dry season in private and communal boreholes

Parameter	**R*f*Ding (µg/kg/day)**	**R*f*Dderm (µg/kg/day)**	**Stats. Parameter**	**Ding (Child)**	**Ding (Adult)**	**HQing (Child)**	**HQing (Adult)**	**CRing (child)**	**CRing (Adult)**	**CDIing (Child)**	**CDIing (Adult)**	**Dderm (Child)**	**Dderm (Adult)**	**HQderm (Child)**	**HQderm (Adult)**
As	3.0E-01		Min	3.6E-01	9.4E-02	2.7E+02	1.2E+02	2.4E-04	6.3E-05	3.6E-01	9.4E-02	1.3E-03	7.7E-04	2.3E+02	3.9E+02
			Max	3.6E-01	9.4E-02	2.7E+02	1.2E+02	2.4E-04	6.3E-05	3.6E-01	9.4E-02	1.3E-03	7.7E-04	2.3E+02	3.9E+02
Fe	7.0E+02	1.4E+02	Min	8.1E-06	4.6E-04	1.2E-01	2.3E+06	ND	ND	1.7E-03	4.6E-04	6.4E-06	2.0E-10	1.0E+07	3.3E+11
			Max	8.1E-06	4.8E-03	1.2E-01	2.3E+06	ND	ND	1.8E-02	4.8E-03	6.8E-05	2.1E-09	1.1E+08	3.6E+12
Cr	3.0E+00		Min	3.4E+00	8.8E-01	1.4E+02	6.1E+01	6.7E-03	9.3E-03	3.4E+00	8.8E-01	2.5E-02	1.4E-02	8.8E+01	1.5E+02
			Max	4.7E+00	1.2E+00	1.4E+02	6.1E+01	1.8E-03	2.4E-03	4.7E+00	1.2E+00	3.4E-02	2.0E-02	1.2E+02	2.1E+02
Mn	2.4E+01		Min	3.4E-01	8.8E-02	2.7E+02	1.2E+02	ND	ND	3.4E-01	8.8E-02	1.2E-03	7.2E-04	2.1E+03	3.7E+03
			Max	3.1E+00	8.0E-01	2.7E+02	1.2E+02	ND	ND	3.1E+00	8.0E-01	1.1E-02	6.5E-03	2.0E+04	3.3E+04
Co	2.0E+01		Min	3.7E-02	9.6E-03	2.7E+01	1.2E+01	ND	ND	3.7E-02	9.6E-03	1.3E-03	7.9E-04	4.2E+03	7.2E+03
			Max	1.3E-01	3.4E-02	2.7E+01	1.2E+01	ND	ND	1.3E-01	3.4E-02	4.7E-03	2.8E-03	1.5E+04	2.5E+04
Ni	2.0E+01		Min	2.3E+00	6.0E-01	2.7E+02	1.2E+02	ND	ND	2.3E+00	6.0E-01	8.4E-03	4.9E-03	5.2E+03	8.8E+03
			Max	3.7E+01	9.7E+00	2.7E+02	1.2E+02	ND	ND	3.7E+01	9.7E+00	1.4E-01	7.9E-02	5.2E+03	1.4E+05
Cu	4.0E+01		Min	1.4E-01	3.8E-02	2.7E+02	1.2E+02	ND	ND	1.4E-01	3.8E-02	5.3E-04	3.1E-04	4.0E+03	6.9E+03
			Max	2.7E+00	7.1E-01	2.7E+02	1.2E+02	ND	ND	2.7E+00	7.1E-01	1.0E-02	5.8E-03	4.0E+03	1.3E+05
Zn	3.0E+01		Min	2.1E+00	5.5E-01	4.5E+02	2.0E+02	ND	ND	2.1E+00	5.5E-01	4.6E-03	2.7E-03	1.1E+03	1.9E+03
			Max	1.2E+01	3.1E+00	4.5E+02	2.0E+02	ND	ND	1.2E+01	3.1E+00	2.6E-02	1.5E-02	1.1E+03	1.1E+04
Cd	1.0E+00		Min	1.1E-02	2.8E-03	2.7E+02	1.2E+02	1.7E-06	4.5E-07	1.1E-02	2.8E-03	4.0E-05	2.3E-05	1.3E+04	2.2E+04
			Max	1.1E-02	2.8E-03	2.7E+02	1.2E+02	1.7E-06	4.5E-07	1.1E-02	2.8E-03	4.0E-05	2.3E-05	1.3E+04	2.2E+04
Hg	2.0E+02		Min	1.7E-01	4.4E-02	2.7E-01	1.2E-01	2.7E-05	7.0E-06	1.7E-01	4.4E-02	6.2E-01	3.6E-01	3.2E-01	5.4E-01
			Max	2.6E-01	6.8E-02	2.7E-01	1.2E-01	4.1E-05	1.1E-05	2.6E-01	6.8E-02	9.5E-01	5.6E-01	4.9E-01	8.3E-01
Pb	3.5E+00		Min	2.9E-02	7.7E-03	6.8E+01	3.1E+01	3.5E-03	9.1E-04	2.9E-02	7.7E-03	4.3E-04	2.5E-04	4.6E+02	7.9E+02
			Max	2.1E-01	5.4E-02	6.8E+01	3.1E+01	2.4E-02	6.4E-03	2.1E-01	5.4E-02	3.0E-03	1.8E-03	4.6E+02	5.6E+03

Table 5.4: The Maximum and minimum values for selected heavy metals of human health risk assessment for wet season in private and communal boreholes

Parameter	R*f*Ding (µg/kg/day)	R*f*Dderm (µg/kg/day)	Stats. Parameter	Ding (Child)	Ding (Adult)	HQing (Child)	HQing (Adult)	CRing (child)	CRing (Adult)	CDIing (Child)	CDIing (Adult)	Dderm (Child)	Dderm (Adult)	HQderm (Child)	HQderm (Adult)
As	3.0E-01		Min	2.4E-01	6.3E-02	2.7E+02	1.2E+02	1.6E-04	4.2E-05	2.4E-01	6.3E-02	8.8E-04	5.1E-04	2.3E+02	3.9E+02
			Max	3.6E-01	9.4E-02	2.7E+02	1.2E+02	2.4E-04	6.3E-05	3.6E-01	9.4E-02	1.3E-03	7.7E-04	3.4E+02	5.8E+02
Fe	7.0E+02	1.4E+02	Min	1.1E-05	4.7E-03	1.2E-01	2.3E+06	ND	ND	1.8E-02	4.7E-03	6.6E-05	2.1E-09	7.7E+06	2.5E+11
			Max	1.1E-05	6.5E-03	1.2E-01	2.3E+06	ND	ND	2.5E-02	6.5E-03	9.1E-05	2.8E-09	1.1E+07	3.4E+11
Cr	3.0E+00		Min	3.3E+00	8.6E-01	1.4E+02	6.1E+01	6.6E-03	1.7E-02	3.3E+00	8.6E-01	2.4E-02	1.4E-02	4.7E+01	8.0E+01
			Max	8.7E+00	2.3E+00	1.4E+02	6.1E+01	1.7E-03	4.6E-03	8.7E+00	2.3E+00	6.4E-02	3.7E-02	1.2E+02	2.1E+02
Mn	2.4E+01		Min	2.0E-01	5.1E-02	2.7E+02	1.2E+02	ND	ND	2.0E-01	5.1E-02	7.2E-04	4.2E-04	2.7E+03	4.6E+03
			Max	2.4E+00	6.4E-01	2.7E+02	1.2E+02	ND	ND	2.4E+00	6.4E-01	8.9E-03	5.2E-03	3.3E+04	5.7E+04
Co	2.0E+01		Min	2.9E-02	7.7E-03	2.7E+01	1.2E+01	ND	ND	2.9E-02	7.7E-03	1.1E-03	6.3E-04	2.9E+03	5.0E+03
			Max	1.9E-01	4.9E-02	2.7E+01	1.2E+01	ND	ND	1.9E-01	4.9E-02	6.9E-03	4.0E-03	1.9E+04	3.2E+04
Ni	2.0E+01		Min	2.0E+00	5.1E-01	2.7E+02	1.2E+02	ND	ND	2.0E+00	5.1E-01	7.2E-03	4.2E-03	4.0E+04	6.8E+04
			Max	4.8E+00	1.3E+00	2.7E+02	1.2E+02	ND	ND	4.8E+00	1.3E+00	1.8E-02	1.0E-02	4.0E+04	1.7E+05
Cu	4.0E+01		Min	3.2E-01	8.3E-02	2.7E+02	1.2E+02	ND	ND	3.2E-01	8.3E-02	1.2E-03	6.8E-04	4.5E+03	7.6E+03
			Max	2.4E+00	6.4E-01	2.7E+02	1.2E+02	ND	ND	2.4E+00	6.4E-01	9.0E-03	5.2E-03	4.5E+03	5.9E+04
Zn	3.0E+01		Min	2.2E+00	5.8E-01	4.5E+02	2.0E+02	ND	ND	2.2E+00	5.8E-01	4.9E-03	2.9E-03	1.0E+03	1.8E+03
			Max	1.3E+01	3.5E+00	4.5E+02	2.0E+02	ND	ND	1.3E+01	3.5E+00	2.9E-02	1.7E-02	1.0E+03	1.1E+04
Cd	1.0E+00		Min	1.2E-03	3.1E-04	2.7E+02	1.2E+02	1.9E-07	5.0E-08	1.2E-03	3.1E-04	4.4E-06	2.6E-06	1.3E+04	2.2E+04
			Max	1.1E-02	2.8E-03	2.7E+02	1.2E+02	1.7E-06	4.5E-07	1.1E-02	2.8E-03	4.0E-05	2.3E-05	1.3E+04	1.9E+05
Hg	2.0E+02		Min	1.3E-01	3.4E-02	2.7E-01	1.2E-01	2.1E-05	5.4E-06	1.3E-01	3.4E-02	4.8E-01	2.8E-01	1.3E-01	2.2E-01
			Max	6.5E-01	1.7E-01	2.7E-01	1.2E-01	1.0E-04	2.7E-05	6.5E-01	1.7E-01	**2.4E+00**	**1.4E+00**	6.3E-01	1.1E+00
Pb	3.5E+00		Min	2.5E-02	6.5E-03	6.8E+01	3.1E+01	2.9E-03	7.6E-04	2.5E-02	6.5E-03	3.6E-04	2.1E-04	1.9E+02	3.3E+02
			Max	5.0E-01	1.3E-01	6.8E+01	3.1E+01	5.8E-02	1.5E-02	5.0E-01	1.3E-01	7.3E-03	4.3E-03	1.9E+02	6.6E+03

Children's chronic daily intake was higher when compared to adults, which suggest that children are more prone to potential health risk associated with the consumption of trace metals in groundwater which is supported by similar studies such as Edokpayi at al. (2018a) and Durowoju *et al*. (2020).

The average values of non-carcinogenic health risk assessment for trace metals in groundwater samples collected from schools and household during the assessment of the study has been shown in appendix Tables 5.1 and 5.2. For the adult population, the calculated values for HI (summation of the HQs) were 9.6E-1 in school samples and 1.0E+00 in household and communal borehole (Table 5.5.). For the children population, the calculated values for HI were >2.2E+00 in school samples and >2.2E+00 in household and communal borehole (Table 5.5). Hence, household with communal water samples had slight similar HI values as compared to samples collected from schools.

The parameters that were identified as the main contributors to non-carcinogenic health risks for both adult and children throughout the study period in all samples collected from schools, private household and communal sites were Cr, Hg, and As with HI values which range from 1.4E-01 to 1.0E+00. Durowoju et al. (2020) reported Hazard Index values higher than 1 for both children and adults in geothermal springs within Soutpansberg region of Limpopo Province in South Africa which correspond with the outcomes of this study.

In general, the health risk assessment index, using the overall non-carcinogenic risk assessment (∑HI), and HQ via ingestion and dermal adsorption routes, were greater than 1 in all trace metals except for hazard quotient value for Hg throughout the assessment. CRing values of Cr and Pb for both age group were $>10^{-4}$ throughout the assessment. This implies that the consumption of groundwater in the study area poses severe critical health threats to both children and adults (Naveedullah et al., 2014; Asare-Donkor et al., 2016; Durowoju et al., 2020). Children are more likely to suffer from anaemia, headache, abdominal pain, kidney and brain damage especially in male children, lungs problems, and stomach cancers among others due to the consumption of contaminated groundwater (Muhammad, 2011; Jaishankar et al., 2014; Cao et a., 2019).

Table 5.5 Summary of average HI values of groundwater of Collins Chabane and Makhado municipality.

School Samples					**Household and Communal water sources**			
	Dry Season		**Wet Season**		**Dry Season**		**Wet Season**	
	HQing/HQderm_Child	**HQing/HQderm_Adult**	**HQing/HQderm_Child**	**HQing/HQderm_Adult**	**HQing/HQderm_Child**	**HQing/HQderm_Adult**	**HQing/HQderm_Child**	**HQing/HQderm_Adult**
Fe	4.5E-14	8.6E-07	3.57E-13	6.89E-06	1.3E-13	2.5E-06	3.67E-13	7.08E-06
V	*	*	*	*	*	*	*	*
Cr	8.6E-01	3.8E-01	1.01E+00	4.51E-01	7.7E-01	3.4E-01	9.32E-01	4.18E-01
Mn	1.3E-01	5.8E-02	2.23E-02	1.00E-02	2.4E-02	1.1E-02	2.06E-02	9.21E-03
Co	1.5E-03	6.6E-04	1.62E-03	7.26E-04	1.8E-03	7.9E-04	2.01E-03	9.01E-04
Ni	7.6E-02	3.4E-02	1.41E-01	6.32E-02	1.4E-01	6.3E-02	8.18E-02	3.67E-02
Cu	4.7E-03	2.1E-03	1.29E-02	5.79E-03	1.0E-02	4.7E-03	1.72E-02	7.72E-03
Zn	6.5E-02	2.9E-02	6.53E-02	2.92E-02	9.5E-02	4.3E-02	9.27E-02	4.15E-02
Cd	9.5E-03	4.3E-03	8.79E-03	3.94E-03	1.3E-02	5.7E-03	4.07E-03	1.82E-03
Hg	4.0E-01	1.8E-01	3.16E-01	1.42E-01	3.5E-01	1.6E-01	4.97E-01	2.23E-01
Pb	2.2E-02	9.7E-03	2.74E-02	1.23E-02	3.8E-02	1.7E-02	6.65E-02	2.98E-02
Al	*	*	*	*	*	*	*	*
As	7.3E-01	3.3E-01	6.19E-01	2.78E-01	7.0E-01	3.1E-01	5.26E-01	2.36E-01
∑HI	2.30E+00	1.03E+00	2.22E+00	9.96E-01	2.15E+00	9.62E-01	2.24E+00	1.00E+00

Table 5.6 Statistical description of HI values for groundwater samples of Collins Chabane and Makhado municipality.

	School samples					Household and communal samples			
	Dry season		Wet season			Dry season		Wet season	
S/N	HI Child	HI Adult	HI Child	HI Adult	S/N	HI Child	HI Adult	HI Child	HI Adult
S1	4.40	1.59	4.80	1.62	**P1**	2.08	0.90	2.91	1.17
S2	5.35	1.85	3.71	1.34	**P2**	2.45	0.98	2.91	1.12
S3	4.32	1.58	3.50	1.37	**P3**	2.61	1.05	2.38	0.95
S4	3.69	1.39	2.86	1.13	**P4**	3.11	1.20	2.91	1.11
S5	3.20	1.26	2.75	1.09	**P5**	3.16	1.20	2.94	1.14
S6	3.08	1.22	3.16	1.20	**P6**	2.68	1.09	2.27	0.93
S7	3.34	1.28	2.90	1.13	**P7**	2.58	1.03	2.59	1.05
S8	3.34	1.32	2.90	1.12	**P8**	3.51	1.30	2.96	1.17
S9	3.10	1.21	2.61	1.04	**P9**	3.08	1.23	3.55	1.28
S10	2.82	1.12	2.61	1.05	**P10**	3.30	1.25	4.91	1.95
S11	2.73	1.11	3.38	1.31	**P11**	3.20	1.23	*	*
S12	3.74	1.45	3.02	1.17	**P12**	3.70	1.39	*	*
S13	3.33	1.28	3.32	1.24	**P13**	3.00	1.15	*	*
S14	2.99	1.19	2.75	1.05	**P14**	3.23	1.21	*	*
S15	2.84	1.13	4.36	1.56	**P15**	3.42	1.25	*	*
S16	3.53	1.33	4.18	1.48	**C1**	3.12	1.18	*	*
S17	3.60	1.34	5.05	1.78	**C2**	2.94	1.13	5.79	2.05
S18			4.02	1.49	**C3**	3.72	1.34	2.01	0.89
S19	3.22	1.24	3.24	1.23					
S20	2.96	1.18	4.21	1.54					
Min	2.73	1.11	2.61	1.04	**Min**	2.08	0.90	2.01	0.89
Max	5.35	1.85	5.05	1.78	**Max**	3.72	1.39	5.79	2.05
Mean	3.45	1.32	3.47	1.30	**Mean**	3.05	1.17	3.18	1.23
S.t.d	0.65	0.19	0.74	0.22	**S.t.d**	0.44	0.13	1.11	0.38

5.2.2 Chronic risk assessment (CDI_{ing}) and carcinogenic risk assessment (CR_{ing}) of primary schools

The average estimated minimum and maximum values for CDI for selected heavy metals in groundwater samples collected from the boreholes from schools, household and communal sites via ingestion pathway for both children and adults are shown **Table 5.1-5.4.** The maximum CDI values for the selected metals for children and adult in dry season ranged between 1.10E-03-9.50E+00 and 2.80E-04-2.50E+00 (Table 5.1) meanwhile estimated index in wet season ranged between 1.20E-03-3.70E+01 and 3.10E-04-9.70E+00 (Table 5.2), respectively.

The CDI indices for heavy metals for school samples during the study period for both age group were found to be in descending order of Mn>Cr>Zn>Ni>As>Cu>V>Hg>Pb>Co>Cd>Al>Fe in dry season and Cr>Ni>Zn>Mn>Cu>As>V>Hg>Pb>Co>Al>Fe>Cd in wet season. The high CDI values of Mn were observed for all age group in dry season, while high estimated values for children ingesting Ni and Zn were observed throughout the study. Moreover, high risk values for both children and adult ingesting Ni and Cr were observed during both wet and dry season in school samples.

Gamvroula et al. (2013) reported dispersal of heavy metals such as Ni, Cr, and Mn due to bedrock weathering influenced through overexploitation of groundwater utilised for agricultural purpose such as for irrigation and for drinking purpose in Attica region, Greece. This study suggests natural factors such as weathering of rock and dissolution of mineral as the major contributors of Ni, Cr and Mn levels in groundwater. However, anthropogenic activities can cause high elevation of this metals such as incidental contact of water in the boreholes with the sewage waste (including leachates from pit latrine toilet) which may cause high concentration of Mn (British Columbia, 2007b). As a results, critical stain and taste problems could occur to be experienced by consumers (DWAF, 1996; WHO, 2006; Edokpayi et al., 2018b; Odiyo et al., 2020). The carcinogenic risk (CRing) associated with the groundwater of the study area was estimated for Cr, Cd, Hg, Pb and As (Tables 5.1 – 5.4).

The CRing values ranged between 5.70E-07 to 1.50E-02 and 1.50E-07 to 1.30E-02 for child and adult during dry season respectively, while 1.90E-07 to 4.10E-02 and 5.00E-08 to 1.60E-02 for child and adult during wet season, respectively (Table 5.1 and 5.2).

In this study, the maximum carcinogenic indices values of Hg ranged between 2.20E-05-4.70E-05 and 5.70E-06-1.20E-05 for both children and adult, throughout the season (Table 5.1), respectively which fell within the recommended limit of <1E-04 for carcinogenic indices as outlined by EPA (1989). Furthermore, As (1.60E-04-2.70E-04) exceeded the regulatory levels for child throughout the season (Table 5.1-5.2). The calculated values of CRing for Cd (5.00E-08-1.70E-06) for all age group throughout the study were low. As presented in Table 5.1 and 5.2, the values of Pb and Cr were above the recommended range (1E-06-1E-04) outline by USEPA (1989) throughout the season. Hence, this study reveals that Cr and Pb could be potential risk to both children and adults; therefore, preventive measure should be implemented.

The estimated average levels of carcinogenic risk (CRing) for As, Cr, Cd, Hg and Pb determined for both children and adult in dry season were in the range of 1.30E-06-8.80E-03 and 8.60E-06-2.30E-03, respectively.

Meanwhile during wet season, the levels were in the range of 11.20E-06-1.00E-02 and 3.10E-07-2.70E-03, respectively (Table 5.7).The maximum and average Cr and Pb level for both children and adult exceeded the target of carcinogenic risk values of 1E-04 throughout the study. Reports have shown that chronic Pb exposure can cause high blood pressure, anaemia, headache, abdominal pain, kidney and brain damage in male, lung, and stomach cancers and high blood pressure especially in adult and elderly individual (Muhammad, 2011; Jaishankar et al.,2014; Cao et al., 2019).

Table 5.7: The assessed average Carcinogenic risk values for public primary schools boreholes during dry and wet season.

	Dry season		**Wet season**	
	CRing (Child)	**CRing (Adult)**	**CRing (Child)**	**CRing (Adult)**
Cr	**8.8E-03**	**2.3E-03**	**1.0E-02**	**2.7E-03**
Cd	1.3E-06	3.4E-07	1.2E-06	3.1E-07
Hg	3.3E-05	8.6E-06	2.6E-05	6.7E-06
Pb	**6.1E-03**	**1.6E-03**	**7.7E-03**	**2.0E-03**
As	2.5E-04	6.6E-05	2.1E-04	5.6E-05

5.2.3 The chronic risk assessment (CDI_{ing}) and carcinogenic risk assessment (CR_{ing}) of private and communal boreholes throughout the season

The average estimated minimum and maximum values for CDI for selected heavy metals in groundwater samples collected from the boreholes from communal and private sites via ingestion pathway for both children and adults are shown Table 5.3-5.4. The maximum CDI values for the selected metals for children and adult in dry season ranged between 1.70E-03-3.70E+01 and 4.60E-04-9.70E+00 (Table 5.3) meanwhile the index during wet season was 1.20E-03-1.30E+01 and 3.10E-04-3.50E+00 (Table 5.4), respectively.

The CDI indices for trace metals for private household and communal samples during the study period for both age group were found to be in descending order of Zn >Ni>Cr>Mn>Cu>As>V>Hg>Pb>Co>Cd>Al>Fe in dry season and Cr>Zn>Ni>Cu>Mn>As>Hg>V>Pb>Co>Al>Fe>Cd in wet season. The high CDI values of Cr, Ni and Zn were estimated for all age group during dry season, also high estimated values for ingesting Zn and Cr were observed in wet season.

Furthermore, high risk values for children ingesting Cu and Ni were evaluated for the wet season. Groundwater interacting with surface water due to high infiltration of rainwater carrying Zn and Cu particles from automobiles (Małecki et al., 2017; Edokpayi et al., 2018b) can cause elevation of these metals in groundwater. However, all boreholes water has slight to no health effects due to Zn since it is known to have antioxidant properties that protect humans against accelerated aging of muscles and skin (Edokpayi et al., 2018b). It also assists in healing process for injured individual if recommended quantity is consumed (Asare-Donkor et al., 2016). Wu et al. (2009) and Naveedullah et al. (2014) reported agricultural practices, use of fungicides and fertilizers being major contributors of high content of Zn and Mn in groundwater quality which could be same source of Zn and Mn content in this study since resident practice agricultural farming in their yard.

The carcinogenic risk assessment (CR_{ing}) for private and communal boreholes was estimated for Cr, Cd, Hg, Pb and As presented in Table 5.3-5.4. The CRing values ranged from 1.70E-06 to 2.40E-02 and 4.50E-07 to 9.30E-03 for child and adult during dry season respectively, while 1.90E-07 to 5.80E-02 and 5.00E-08 to 1.70E-02 for child and adult during wet season, respectively (Table 5.3 and 5.4). Cr and Pb were obtained at the range between 7.60E-04 to 5.80E-02 throughout the assessment in both age group while, As was obtained at 1.60E-04 to 2.40E-04 in child group throughout the study period. Edokpayi et al. (2018a) reported similar results of CRing values for Pb which ranged from 1.16E−04 to 3.55E−04 and 3.05E−05 to 9.29E−05 for children and adults, respectively. This values were beyond the recommended range of 1E-06 - 1E-04 by EPA (1989). Cd and Hg (5.00E-08 to 1.00E-04) complied with EPA (1989) guideline values of CRing throughout the study period.

The values of Cd (1.90E-07-1.70E-06 and 5.00E-08-4.50E-07) were obtained to be low for children and adult (Table 5.3-5.4), respectively throughout the study period According to USEPA (1989), cancer risks that are below 1E-06 are considered very low i.e., negligible. Thus, the risk of developing cancer from Cd due to ingestion from all sampled sites can be considered as negligible. Meanwhile, on average there is a possibility of 5 persons in every 10^6 developing cancer due to lifetime exposure to Cr and Pb through ingestion of groundwater at the study area. As referred from Table 5.8 below, Cr and Pb were obtained with average values which were above 1E-04 and 1E-06 as recommended by EPA (1989) during the course of study. Hence, this study reveals that Cr and Pb could pose potential risk to both children and adults; therefore, preventive measure should be implemented.

Furthermore, the estimated average levels of carcinogenic risk (CR_{ing}) for As, Cr, Cd, Hg and Pb determined for both children and adult in dry season were in the range of 1.70E-06-1.10E-02 and 4.50E-07-2.80E-03, respectively. Meanwhile, during the wet season the levels were in the range of 5.50E-07-1.90E-02 and 1,40E-07-4.90E-03, respectively (Table 5.8).

Generally, apart from Hg, all selected elements had CR_{ing} values above the carcinogenic indices of 1E-04 and 1E-06 throughout the study. Edokpayi et al. (2018b) reported high estimated CR_{ing} values of Cr and Pb in the groundwater sampled from household and communal borehole in Muledane area of Vhembe district in South Africa, This study is similar with findings of Edokpayi et al. (2018b) in terms of CR_{ing} levels for Cr and Pb in the groundwater. These toxic metals could pose possible health risk to residence in the investigated area. Therefore, precaution needs to be taken into consideration to avoid possible CR_{ing} of residence of residing in the study area especially, children utilising the borehole water. Kotaś and Stasicka (2000) and Hitkovich (2011) reported that Cr as natural occurring element which could originate from various sources either anthropogenic or natural with high environmental flexibility.

Table 5:8: The estimated average Carcinogenic risk values for dry and wet season in both private and communal boreholes

	Dry season		**Wet season**	
Element	**CR_{ing} (child)**	**CR_{ing} (Adult)**	**CR_{ing} (child)**	**CR_{ing} (Adult)**
Cr	**7.9E-03**	**2.1E-03**	**9.6E-03**	**2.5E-03**
Cd	1.7E-06	4.5E-07	5.5E-07	1.4E-07
Hg	2.9E-05	7.6E-06	4.0E-05	1.1E-05
Pb	**1.1E-02**	**2.8E-03**	**1.9E-02**	**4.9E-03**
As	2.4E-04	6.3E-05	1.8E-04	4.7E-05

5.3 Microbial Risk Assessment

Based on existing literature, *E. coli* is one of the commonly used pathogens in QMRA which is well known to cause infections and illnesses (Machdar et al., 2013, Ahmed et al., 2020). Contamination of groundwater with pathogenic strains of *E. coli* make groundwater hazardous. The results of water quality analysis disclosed that 100, 50 and 6.67% of groundwater from communal, primary schools and household borehole sites had risks associated with pathogenic infections due to consumption of contaminated groundwater with *E. coli*.

The range of ingested doses of *E. coli* from communal, household and school borehole were 0.00E+00-8.00E-02, 0.00E+00-2.77E+00 and 0.00E+00-2.67E+01 CFU/day (Table 5.9). The mean value across all schools, households and communal sites were 1.81E+00, 1.85E-01 and 5.78E-02 CFU/day. The outcome of this values suggest that school boreholes had higher risk of infection compared to household and communal sites. The highest ingested doses for *E. coli* from schools, households and communal sites were obtained from S17, P13 and C1.

The average ingested doses for *E. coli* obtained by Ahmed et al. (2020) and Odiyo et al. (2020) in two districts (northern and central Sindh districts) in India and Vhuronga 1 region of Limpopo Province in South Africa ranged from 3.31–92.5 and 0.00–2.50 CFU/day, respectively. Higher levels of *E. coli* were observed in the groundwater of schools in this study than those reported by Odiyo et al. (2020). Furthermore, obtained values for communal groundwater were lower than those obtained by other studies (Ahmed et al., 2020; Odiyo et al., 2020). Health effects of *E. coli* pathogenic strain in schools (S3, S6, S8, S10, S11, S12, S15, S16, S17 and S18), household sample P13 and all communal samples could cause illness be such as nausea, fever, vomiting, headaches, abdominal cramps and chills (WHO, 2011).

The maximum risks values of infection per day for children in schools were 4.96 (S12), 6.67 (S15) and 28.74% (S17) during the month August, October and November in 2019 respectively (Fig. 5.1a). Meanwhile for adult it was obtained at 34.81(S12), 31.62 (S12) and 43.14% (S17) August, October and November in 2019, respectively (Fig. 5.1b). The month of November has the highest risk of infection as compared to other months. This could be due to more waste from concentrated livestock and sewage infiltrating the ground since November was wet season while August and October were dry season in the study area. All household and communal samples had zero E.*coli* in the month of November. The maximum risks values of infection per day for children in household were obtained during the month of August (12.96%) and October (7.58%) while for adult were 35.32 (August) and 32.00% (October) in P13 site. The maximum risks values of infection for communal site were low during August in 2019 with 0.88 for Children and 22.44% for Adult for both C1 or C2 borehole site (Fig. 5.1c and d).

Table 5.9: The computed average ingested dose of bacteria (CFU/day) of Collins Chabane and Makhado municipality throughout the assessment

Sample ID	Mean (cfu/100 mL)	S.t.d	Average Dose ingested *E.coli*	Sample ID	Mean (cfu/100 mL)	S.t.d	Average Dose ingested *E.coli*
S1	0.00	0.00	0.00	**P1**	0.00	0.00	0.00
S2	0.00	0.00	0.00	**P2**	0.00	0.00	0.00
S3	1.00	1.73	0.08	**P3**	0.00	0.00	0.00
S4	0.00	0.00	0.00	**P4**	0.00	0.00	0.00
S5	0.00	0.00	0.00	**P5**	0.00	0.00	0.00
S6	0.33	0.58	0.03	**P6**	0.00	0.00	0.00
S7	0.00	0.00	0.00	**P7**	0.00	0.00	0.00
S8	0.67	1.15	0.05	**P8**	0.00	0.00	0.00
S9	0.00	0.00	0.00	**P9**	0.00	0.00	0.00
S10	5.00	8.66	0.40	**P10**	0.00	0.00	0.00
S11	2.67	4.62	0.21	**P11**	0.00	0.00	0.00
S12	93.33	86.07	7.47	**P12**	0.00	0.00	0.00
S13	0.00	0.00	0.00	**P13**	34.67	38.44	2.77
S14	0.00	0.00	0.00	**P14**	0.00	0.00	0.00
S15	7.67	13.28	0.61	**P15**	0.00	0.00	0.00
S16	4.00	6.08	0.32	**C1**	1.00	1.41	0.08
S17	333.33	577.3	26.67	**C2**	0.67	1.15	0.05
S18	3.33	5.77	0.27	**C3**	0.50	0.71	0.04
S19	0.00	0.00	0.00				
S20	0.00	0.00	0.00				

This study further used QMRA technique, to predict the probability of infection and illness per annum in the community of the study area population due to exposure to microbiologically unsafe water. Most of the school sites (35%, n= 20) i.e., S10- S12 and S15-S18, had an extremely high annual risk of *E. coli* infections to children with computed percentage of 90.52-100 and 94.48-100% respectively with the highest obtained values of 100% at S12 and S17 for all age group (Fig. 5.2a). The annual risk of illness per year for school followed the same trend with lower percentage of 35% in S12 and S17 site (Fig. 5.2b). The annual risk of *E. coli* infections and illness was high in household site P13 with 100% and 35% for all age group, respectively. Meanwhile, 80.94 and 28.33% were the highest maximum values assessed for infection and illness in communal site (C1) (Fig. 5.2 c and d).

Odiyo et al. (2020) recorded the highest risk of infection and illness value per year of 89.11 and 31.19%, in schools, this study found most of schools having higher risk as compared to this previous study. However, the obtained values for risk of infection per year relate to those of Machdar et al. (2013) and Ahmed et al. (2020) with recorded values of 99.7% and 97.9–100%. Ahmed et al. (2020) recorded the high probability risk of illness values per year at the range of 34.9–35%. These are similar to the high values of probability risk of illness obtained in this study.

Moreover, these levels indicate high ingested doses of *E. coli* within the study area which support the findings of Taonameso et al. (2019), Enitan-Folami et al. (2019), Odiyo et al. (2020). Taonameso et al. (2019), reported the presence of E. coli (> 10 per 100 mL) in 25% of borehole (125 number of samples) sampled within the locality of Vhembe district municipality. Furthermore, Ahmed et al. (2020) reported half (49%) of the drinking-water samples being contaminated with *E.* coli (49%) in Sindh province of Pakistan.

Odiyo and Makungo (2018), Enitan-Folami et al. (2019), Odiyo et al. (2020) among others reported the pervasiveness of diarrhea infection due to consumption of groundwater contaminated with *E. coli* in Vhembe District Municipality. This designates that these diarrhoeagenic pathogens are the main threat to the health of rural communities and primary schools within the District. Hence, there is a need to protect groundwater sources from microbial contamination. *E. coli* is well-known cause gastrointestinal diseases worldwide (Takal and Quaye-Ballard, 2018).

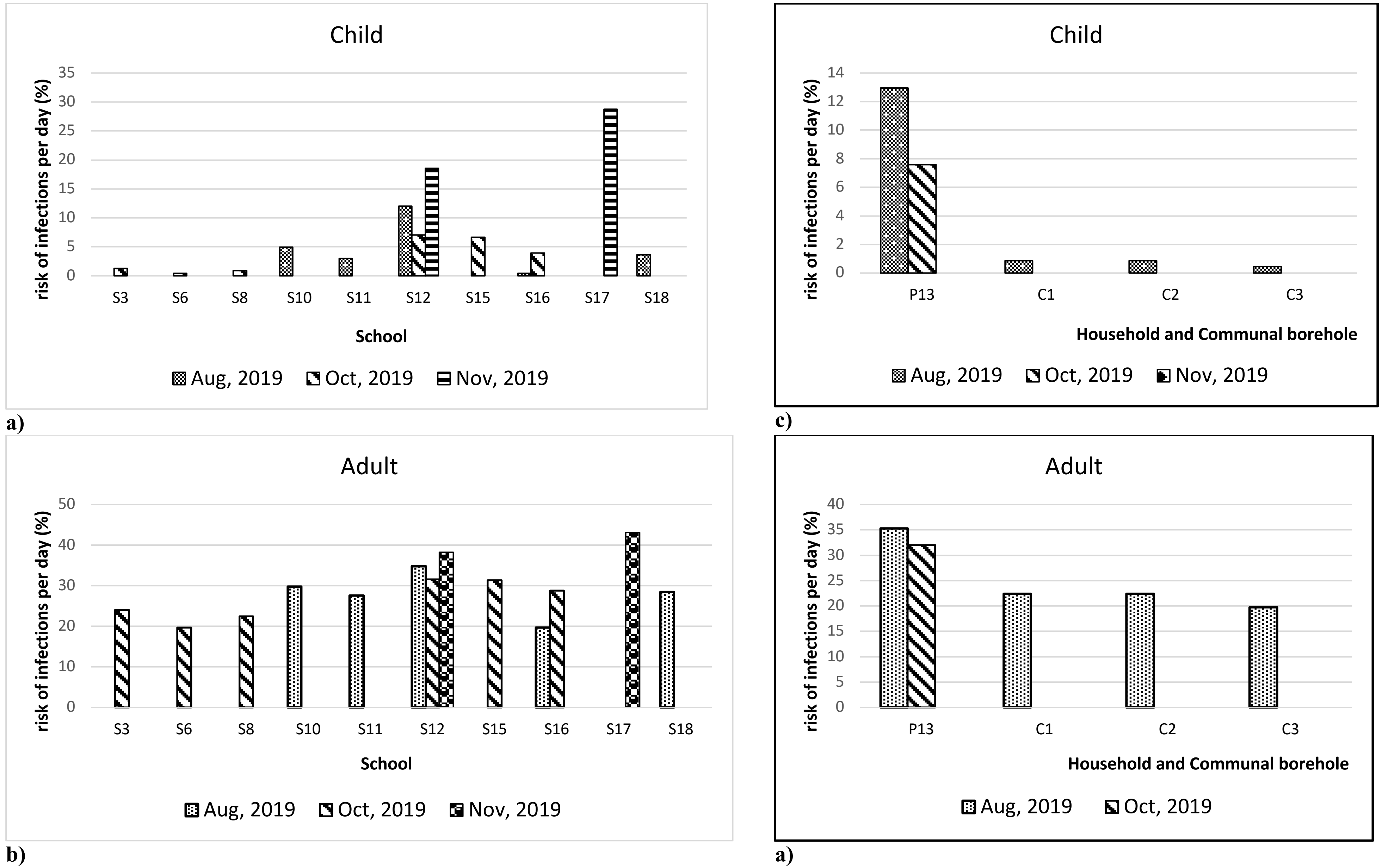
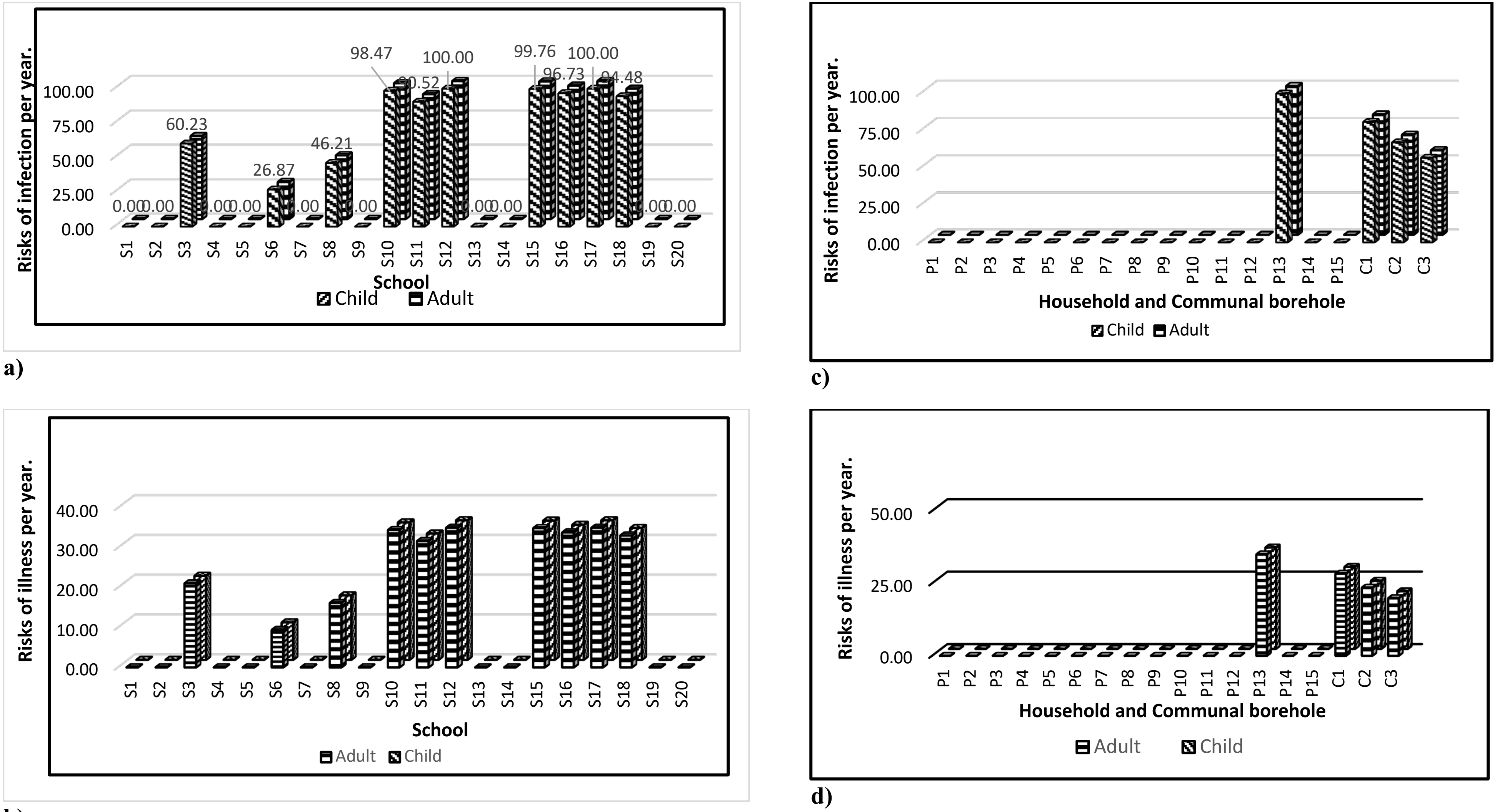


Figure 5.1 Risk probability of infection per day for school, household



a)

c)

b)

d)

Figure 5.2. The risk probability of infection per year for school, household and communal water samples of Collins Chabane and Makhado Municipality.

5.4 Conclusion

Drinking of contaminated groundwater by humankind poses serious health risk through dermal contact and direct ingestion. The non-carcinogenic risk classification in drinking groundwater indicates that children are at a greater risk due to heavy metals especially Cr, Zn and Ni followed by adults being the least affected in the study area.

The levels of Cr, Zn and Ni in each sampling location was higher than that of Mn, Cu, As, V, Hg, Pb, Co, Al/Fe and Cd. Natural processes such as microbial interferences, interaction between contaminated water with Zn particles (above water table) and groundwater during heavy rain fall, and geochemical processes and anthropogenic activities such as disposal of metal products such as a stainless-steel material around the study area could cause high levels of Cr, Zn and Ni in groundwater. Children consuming groundwater from communal and household boreholes are at greater risk to non-carcinogenic exposure through ingestion due to the levels of Cr and Zn recorded. In addition to the estimated metals, the estimated chronic daily intake for Mn among both children and adult were high in dry season for groundwater in schools. The overall non-carcinogenic risk assessment (HI), HQ and CDI via ingestion and dermal adsorption routes, were >1 and 1.0E-04. This imply that groundwater could pose severe non-carcinogenic health threats to both children and adults through the pathways.

The observed CR_{ing} values for Cr and Pb for both age group were high throughout the study. The ingestion pathway was the main pathway that poses serious health risk, due to accumulation of trace metals such as Cr, Ni, Zn, Mn, Pb and As as the core drivers.

The estimation of QMRA indices values suggest that school boreholes had higher risk of infection than household and communal boreholes investigated. This study suspects the amount of waste from concentrated livestock, pit latrine toilets and septic tank located within the vicinity of school boreholes being the major driver of contamination.

Highest risk of infection was observed in November compared to August and October 2019. This could be due to more leaches infiltrating the ground since frequent rain event occurred in November in South Africa. The school borehole site S12 and S17 had annual risk of E. *coli* infection and illness values of 100% and 35% respectively for all age group which may result in nausea, fever, vomiting, headaches, abdominal cramps and chills infection.

The annual risk of *E. coli* infections and illness was high in household site P13 with 100% and 35% for all age group respectively. Meanwhile, 80.94 and 28.33% were the highest maximum values assessed for infection and illness in communal site (C1). Therefore, the estimation of QMRA indices suggest groundwater from schools (S10- S12 and S15-S18), household (P13) and communal (C1) can be injurious to human health.

CHAPTER SIX : GENERAL CONCLUSION AND RECOMMENDATION

Results from this study showed that the measured physico-chemical parameters (pH, EC, TDS, salinity, turbidity, and temperature) in all selected boreholes fell within the recommended standard limits for SANS (2015) apart from private household sample (P6) collected in dry season with recorded pH value of 3.3. Based on the mean concentrations recorded across all samples except S1 and P12, it can be concluded that major anion such as F^-, B, SO_4, Cl^- are within the standard limit during the wet and dry season. However, nitrate concentration obtained was above the standard limit of SANS 241 in most individual household samples, especially during the wet season. Only 55.00, 20.00%, and 66.67% of boreholes in school, household and communal boreholes have the ideal water quality in terms of NO_3^- throughout the study. This study also infers that there could be the risk of methaemoglobinaemia in infants consuming the groundwater on a continuous basis.

A strong positive significant relationship was detected between nitrate and phosphate in household and communal sites, and nitrate and chloride in schools which is evident agricultural activity, sewage contamination as possible sources of contamination. Only 1 of 15 household site (P12) had high concentration of Cl^- throughout the study period which can noticeably affect taste in groundwater from the source due to chloride concentration.

Only one school (5%) site (S1) have been noticed with high concentration of F^-. Since there is no evidence of anthropogenic sources of fluoride contamination, this study suggests that natural occurring activities such as weathering and leaching of fluoride-bearing minerals from rocks and sediments are the possible source of the contamination.

Most samples did not comply with standard limit of SANS 241 and DWAF 1996 in terms of Ca and Mg which reveals that groundwater can cause scaling effect if used on water boilers. The fitness of drinking water in terms of anions investigated in descending order is as follows: Boron > Sulphate > Fluoride > Chloride> Nitrate and cations in the order of K > Na > Ca > Mg. The concentration of heavy metals such as As, Sb, Cd, Bi, Co, Hg, Pb and U were detected in low concentration across all samples, meanwhile the concentration of Zn, Mn, V and Cu complied with SANS 241 and WHO standard guideline. Al, Cr and Ni were above the permissible limit set by SANS 241 and WHO. High concentrations of Al gradually increased during the wet season, similarly the same trend was recorded from Cr and Mg concentrations in this study while Ni opposes trend. Hence, consumption of groundwater without prior treatment from these boreholes during wet season can have negative health impact such as renal failure and Alzheimer's disease infection.

According to piper plot, the groundwater water was dominated by Mg, HCO_3 and Cl ions which makes the groundwater type Ca-Mg-HCO_3 and Mg-Cl water type. The concentration of greater than 180 mg/L of total hardness was observed in 91.83% (n= 73) of samples. This denotes that the water is hard in nature and originate from/within carbonic rock and magnesite mineral. Generally, samples collected from Collins Chabane and Makhado municipality were dominated by Mg-HCO_3 and Mg-Cl water type, respectively.

The WQI value of the selected schools (50-103 and 25-101), household (26-485 and 21-442) and communal (35-57 and 50-56) borehole during dry and wet season respectively fell between the excellent to poor, excellent to unsuitable and excellent to good water based on the parameters used, respectively. In this study, the WQI identified four category class (excellent, good, poor and unsuitable). Based on considered chemical parameters, all school groundwater sources (85%, n= 19) were fit for domestic use in dry season except for groundwater source S2 while 80% (n= 20) and 15% (n= 20) were suitable for drinking and domestic purposes in wet season.

About 40% (n=15) and 50% (n=14) of household water samples collected in dry season and wet season respectively were fit for domestic purposes. Moreover, low percentage (13.33% and 7.14%) observed from household in dry and wet season suggest that the groundwatwe were not suitable for domestic use. All communal groundwater samples were fit for drinking purpose in dry season except C2 which was only fit for domestic purposes while in wet season, the communual boreholes were only suitable for domestic purposes.

Although 15.07% of samples were not suitable for domestic use in this study, the water quality could possibly worsen if well-timed actions for their management are not taken. Nitrate was the principal element with enormously high concentrations that violated the WHO and SANS 241 permissible limit for drinking purpose thus caused high WQI levels. Based on observation of water sources, contamination could be due to anthropogenic activities, especially inorganic fertilizer which includes lawn fertilizers, waste from septic systems, inappropriate setting of pit latrine toilet, concentrated domestic animals in residential area (animal manure), washing of cars and laundry within the vicinity where the boreholes were found.

The microbial analysis results showed that groundwater at selected villages in Vhembe district is contaminated with *E. coli* and total coliforms especially during the wet season. All borehole water samples did not comply with SANS 241 and WHO `during the course of the study apart from private household (P3-P5) samples collected in dry season. All borehole categories investigated during wet season are classified in poor water quality that needs proper treatments.

Health risk assessment model were assessed through evaluation of the health risks that heavy metal could pose on children and adult via direct ingestion and dermal adsorption of groundwater in the investigated study. This was achieved by estimations of the EXPs, CDIs, CR_{ing} and HQs of the selected heavy metals. The non-carcinogenic exposure through ingestion reveals that school children are at higher risk due to Cr and Ni in the selected schools. Meanwhile children drinking groundwater in communal, or household boreholes are also at greater risk due to Cr and Zn. In addition, the estimated chronic daily intake for Mn among both children and adult were high in dry season for groundwater in schools. The overall non-carcinogenic risk assessment (HI), HQ and CDI via ingestion and dermal adsorption routes, were greater than 1 and 1.0E-04. This gives a suggestion to conclude that groundwater poses severe critical health threats to both children and adults through the pathways.

Consumption of the investigated boreholes water could pose carcinogenic risk (CR_{ing}) due to Cr and Pb concentration for adults and children. The maximum and average Cr and Pb level for both children and adult exceeded the USEPA target of carcinogenic risk values of 1E-04 throughout the study. The ingestion pathway is the main pathway for humankind, with trace metals such as Cr, Ni, Zn, Mn, Pb and As as core drivers.

The estimation of QMRA indices values suggest that school boreholes had higher risk of infection than household and communal sites. The highest ingested doses for *E. coli* from schools, households and communal sites were obtained from S17, P13 and C1 which may result in nnausea, fever, vomiting, headaches, abdominal cramps and chills infection. Highest risk of infection has been detected during the month of November (wet season) in 2019. Only 30% of school boreholes had an extremely high annual risk (90.52-100% probability) of *E. coli* infections to children. Only 10% of school borehole site (S12 and S17) had 100% and 35% of both annual risk of infection and illness for all age group for school, respectively. The annual risk of *E. coli* infections and illness was high in household site P13 with 100% and 35% for all age group respectively. Meanwhile, 80.94 and 28.33% were the highest maximum values assessed for infection and illness in communal site (C1).

6.1 RECOMMENDATIONS AND FUTURE STUDIES

Routine monitoring of boreholes should be conducted on a regular basis to determine the quality status of the groundwater in the study area. More microbial water quality paramaters should be evaluated in future studies.

More awareness should be provided to the community, school teachers and learners about water management along with the health implications associated with drinking contaminated water. Proper education about sitting of boreholes should be conducted in the study area.

The provision of potable water should be looked into to prevent episode of diseases outbreak while in the meantime point-of use water treatment facilities should be encouraged in the study area. Adequate sanitation facilities should be provided to the school as well as good hygienic routine should be implemented.

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APPENDICES

Appendix Table 3.1: Geographical Location of borehole samples investigated in this study.

Sample	Geographical Location	Sample	Geographical Location
S1	23°11'38.1"S 30°19'44.2"E	**P1**	23°12'20.3"S 30°16'42.5"E
S2	23°12'26.7"S 30°19'57.8"E	**P2**	23°12'24.7"S 30°16'03.8"E
S3	23°11'04.1"S 30°18'43.7"E	**P3**	23°12'33.0"S 30°14'11.7"E
S4	23°10'45.4"S 30°18'24.5"E	**P4**	23°10'30.4"S 30°13'39.7"E
S5	23°10'46.5"S 30°17'50.0"E	**P5**	23°09'40.2"S 30°15'01.0"E
S6	23°09'47.6"S 30°16'08.8"E	**P6**	23°09'58.0"S 30°15'23.6"E
S7	23°09'40.7"S 30°14'42.0"E	**P7**	23°09'57.4"S 30°16'07.3"E
S8	23°10'30.7"S 30°14'03.2"E	**P8**	23°09'52.7"S 30°16'12.8"E
S9	23°09'48.3"S 30°13'37.5"E	**P9**	23°10'06.9"S 30°16'51.9"E
S10	23°10'20.7"S 30°12'33.7"E	**P10**	23°10'24.6"S 30°17'51.0"E
S11	23°09'53.3"S 30°12'38.1"E	**P11**	23°11'52.8"S 30°19'39.2"E
S12	23°11'04.5"S 30°10'32.8"E	**P12**	23°11'11.3"S 30°19'00.2"E
S13	23°11'14.0"S 30°11'05.3"E	**P11**	23°11'06.9"S 30°18'53.5"E
S14	23°11'51.1"S 30°11'20.1"E	**P14**	23°11'06.5"S 30°19'13.7"E
S15	23°12'13.1"S 30°12'04.0"E	**P15**	23°11'25.7"S 30°19'07.8"E
S16	23°12'28.0"S 30°12'33.9"E	**C1**	23°11'56.0"S 30°12'43.9"E
S17	23°12'13.4"S 30°16'31.4"E	**C2**	23°12'26.4"S 30°14'13.9"E
S18	23°12'30.8"S 30°15'16.6"E	**C3**	23°10'03.7"S 30°16'51.4"E
S19	23°12'27.4"S 30°14'04.3"E		
S20	23°11'47.4"S 30°15'50.9"E		

S=School borehole, P=Individual household borehole, C=Communal borehole

Appendix Table 4.1: The set standard guideline values (mg/L) of water quality for drinking water the Republic of South Africa and World Health Organisation.

Parameter	DWAF	WHO Values	SANS 2015
pH	-	$6.5\text{-}8.5^{\#}$	5-9.7
E.C. (Electrical conductivity)	-	-	1700 µS/cm
TDS	-	$500^{\#}$	1200
Cl^- (Chloride)	-	$250^{\#}$	≤ 300
NO_3^- (Nitrate)	-	$50^{\#}$	11 (as N)
NO_2^- (Nitrite)	-	-	0.9
F^- (Fluoride)	-	-	1.5
SO_4^{-2} (Sulphate)	-	250-400	500
Ca (Calcium)	32	-	-
Mg (Magnesium)	-	50^{**}	-
Na (Sodium)	-	-	200
B (Boron)	-	0.3^{**}	2.4
Aluminium (Al)	0.15	0.2^{**}	0.3
Iron (Fe)	0.1	$0.1^{\#}$	2
E. *coli* (cfu/100mL)	0	0	1
Total Coliform (cfu/100mL)	-	-	10

Source: * WHO (1993), $^{\#}$ WHO (2004). pH has no unit

Appendix Table 4.2: Major Anions and Cations in Dry Season in mg/L

Anion in mg/L (Dry Season)	Cl^- (Chloride)	NO_3^- (Nitrate)	**NO_2^- (Nitrite)**	F^- (Fluoride)	SO_4^{-2} (Sulphate)	PO_4^{-3} (Phosphate)	HCO_3^- (Bicarbonate)	Ca (Calcium)	Mg (Magnesium)	K (Potassium)	Na (Sodium)	B (Boron)	**Aluminium (Al)**	**Iron (Fe)**
S1	50.01	69.78	**< 0.02**	2.16	10.36	1.68	860	54.40	62.00	4.56	68.40	0.04	< 0.01	0.02
S2	50.12	60.31	**< 0.02**	1.24	12.21	0.50	912	64.90	79.30	3.67	44.80	0.05	< 0.01	0.02
S3	49.75	56.26	**< 0.02**	0.89	11.85	0.57	576	75.30	57.00	3.76	26.60	0.03	< 0.01	0.02
S4	47.62	12.09	**< 0.02**	0.69	3.47	0.85	431	38.30	33.90	1.75	59.10	0.02	< 0.01	0.01
S5	56.46	62.89	**< 0.02**	0.54	7.35	1.37	74.42	36.20	31.10	1.38	51.50	0.02	< 0.01	0.02
S6	68.58	111.14	**< 0.02**	0.29	17.95	0.32	509	42.30	59.70	10.70	32.00	0.01	< 0.01	0.02
S7	19.98	15.07	**< 0.02**	0.20	4.31	0.50	112	24.30	32.60	4.45	23.50	0.01	< 0.01	0.02
S8	26.48	27.69	**< 0.02**	0.09	4.05	0.42	439	21.30	45.20	5.70	17.80	0.01	< 0.01	0.02
S9	37.98	34.26	**< 0.02**	0.33	10.94	0.7	68.32	31.60	50.70	4.46	33.90	0.05	0.34	0.01
S10	24.76	13.51	**< 0.02**	0.40	9.28	0.37	140	18.40	24.90	5.55	20.50	0.02	0.20	0.01
S11	37.17	7.02	**< 0.02**	0.25	5.72	0.77	159	25.10	33.70	2.76	19.10	< 0.01	0.31	0.08
S12	14.12	9.57	**< 0.02**	< 0.03	2.02	0.28	176	16.10	41.10	2.76	13.60	0.01	< 0.01	0.02
S13	27.50	39.16	**< 0.02**	0.06	6.43	0.07	93.94	26.50	28.00	2.85	20.90	0.01	< 0.01	0.02
S14	67.49	103	**0.05**	0.24	15.24	0.65	110	42.60	44.90	2.01	35.70	0.02	< 0.01	0.02
S15	45.44	28.83	**< 0.02**	< 0.03	8.25	0.42	95.16	28.10	27.40	1.75	37.10	0.01	< 0.01	0.02
S16	35.72	29.84	**< 0.02**	< 0.03	6.53	< 0.01	107	25.70	48.70	3.40	20.00	0.01	< 0.01	0.02
S17	39.05	46.87	**< 0.02**	< 0.03	9.82	0.16	161	31.80	45.80	3.23	28.40	0.02	< 0.01	0.02
S19	66.61	88.93	**< 0.02**	0.28	16.57	0.23	96.99	28.70	56.40	4.78	26.00	0.01	< 0.01	0.02
S20	64	91.48	**< 0.02**	< 0.03	32.91	< 0.01	57.34	35.70	38.40	5.19	31.10	0.01	< 0.01	0.02

P1	39.29	40.71	**< 0.02**	< 0.03	8.46	0.06	98.21	45.50	52.40	2.59	27.60	0.03	< 0.01	0.01
P2	19.16	2.03	**< 0.02**	0.24	5.94	0.04	69.54	21.00	11.40	4.62	17.80	0.03	< 0.01	0.02
P3	63.43	133	**< 0.02**	0.39	37.09	1.09	71.37	29.60	49.90	4.51	47.30	0.02	< 0.01	0.02
P4	19.93	17.52	**< 0.02**	0.14	2.68	0.21	115	18.20	27.10	2.69	18.80	0.02	< 0.01	0.02
P5	35.94	29.73	**< 0.02**	0.30	6.08	0.28	96.38	31.20	37.90	4.71	24.20	0.01	< 0.01	0.01
P6	41.49	**1532**	**< 0.02**	< 0.03	46.30	13.89	0	31.00	39.50	6.14	24.20	0.01	< 0.01	0.03
P7	73.87	192	**< 0.02**	0.46	34.47	0.2	150	51.40	66.80	10.70	42.00	0.03	< 0.01	0.01
P8	88.69	204	**< 0.02**	0.35	12.48	0.2	296	52.10	73.20	12.50	23.50	0.02	< 0.01	0.02
P9	57.07	45.06	**< 0.02**	0.55	12.10	0.07	60.39	48.60	32.90	1.79	31.90	0.01	< 0.01	0.02
P10	75.56	78.76	**< 0.02**	0.45	40.81	0.36	91.50	51.50	36.10	0.49	51.00	0.02	< 0.01	0.02
P11	77.13	158	**< 0.02**	0.87	10.74	< 0.01	279	79.20	72.50	4.73	26.50	0.03	< 0.01	0.02
P12	647	846	**< 0.02**	1.24	45.87	1.38	556	349	309	7.47	67.90	0.26	< 0.01	0.02
P13	50.46	42.24	**< 0.02**	0.90	9.30	1.57	124	57.70	53.10	3.91	22.40	0.03	< 0.01	0.01
P14	67.59	92.87	**< 0.02**	0.91	14.00	< 0.01	123	69.60	56.20	3.05	35.30	0.05	0.29	0.15
P15	89.4	132	**< 0.02**	0.96	8.49	0.30	95.77	70.30	64.40	5.25	28.30	0.03	0.30	0.15
C1	29.43	22.27	**< 0.02**	0.07	4.38	0.19	133	22.00	40.60	3.91	19.10	0.01	0.15	0.15
C2	52.19	74.76	**< 0.02**	0.28	15.14	0.06	72.59	24.70	52.00	7.07	25.60	0.01	0.17	0.15
C3	49.88	26.95	**< 0.02**	0.57	10.53	0.09	210	40.80	31.10	1.76	32.80	0.01	0.22	0.15
P=Private borehole; C=Communal borehole														
Major Anions and Cations in Wet Season in mg/L														

Appendix Table 4.3 : Major Anions and Cations in Wet Season in mg/L

Anion (Wet Season)	Cl^- (Chloride)	NO_3^- (Nitrate)	**NO_2^- (Nitrite)**	F^- (Fluoride)	SO_4^{-2} (Sulphate)	PO_4^{-3} (Phosphate)	HCO_3^- (Bicarbonate)	Ca (Calcium)	Mg (Magnesium)	K (Potassium)	Na (Sodium)	B (Boron)	**Aluminium (Al)**	**Iron (Fe)**
S1	48.87	66.70	**< 0.02**	2.03	10.25	< 0.01	328	51.60	58.90	4.45	63.80	0.04	0.27	0.15
S2	48.64	53.34	**0.05**	1.27	11.55	< 0.01	381	47.70	78.90	3.86	45.10	0.05	0.25	0.16
S3	47.19	38.93	**< 0.02**	0.87	10.43	1.01	204	63.00	50.60	3.58	25.50	0.02	0.28	0.15
S4	52.66	13.03	**< 0.02**	0.65	2.66	0.3	118	36.30	33.30	1.77	65.10	0.02	0.22	0.15
S5	57.68	67.95	**< 0.02**	0.52	7.36	0.11	258	34.70	29.70	1.58	52.90	0.01	0.21	0.15
S6	55.65	91.51	**< 0.02**	0.4	14.33	0.12	86.62	32.70	45.10	12.80	32.70	0.01	0.21	0.15
S7	21.04	14.74	**< 0.02**	0.22	4.04	0.14	101	22.60	31.00	4.37	23.40	0.01	0.16	0.15
S8	27.31	33.99	**< 0.02**	0.03	3.94	0.11	132	19.70	43.70	5.45	18.20	0.01	0.16	0.15
S9	36.62	35.09	**< 0.02**	< 0.03	10.68	0.58	87.84	28.50	48.20	4.31	37.80	0.04	0.19	0.15
S10	25.51	13.35	**< 0.02**	0.26	9.3	0.06	60.39	16.70	24.70	5.52	23.40	0.01	0.14	0.15
S11	37.15	6.92	**< 0.02**	0.15	5.47	< 0.01	61.00	22.30	32.50	2.70	22.60	< 0.01	0.17	0.15
S12	14.70	9.51	**< 0.02**	< 0.03	2.00	0.13	131	14.40	39.70	2.72	15.30	0.01	0.14	0.15
S13	31.03	48.75	**< 0.02**	0.03	6.90	0.04	98.82	26.60	27.90	2.94	22.10	0.01	0.19	0.15

S14	68.96	120	**< 0.02**	< 0.03	21.60	< 0.01	146	42.00	57.40	2.03	29.00	0.01	0.23	0.15
S15	43.83	41.08	**< 0.02**	0.06	7.91	0.05	89.67	24.90	25.30	1.74	36.40	0.01	0.18	0.15
S16	35.13	27.82	**< 0.02**	< 0.03	6.04	0.14	93.33	23.90	46.20	3.36	21.20	0.01	0.18	0.16
S17	40.18	50.13	**< 0.02**	< 0.03	9.43	< 0.01	73.81	31.70	44.30	3.18	29.40	0.01	0.20	0.16
S18	35.61	48.20	**< 0.02**	< 0.03	9.59	0.88	51.85	34.10	38.00	3.93	27.60	0.01	0.22	0.16
S19	64.87	89.63	**< 0.02**	< 0.03	16.31	0	61.61	24.90	53.20	4.98	28.80	0.01	0.18	0.15
S20	58.98	83.64	**< 0.02**	< 0.03	29.7	0.16	39.65	29.40	34.20	5.16	33.80	0.01	0.21	0.15
P1	40.97	36.03	**< 0.02**	< 0.03	8.38	< 0.01	95.16	42.70	51.00	2.58	30.60	0.02	0.24	0.16
P2	110	195	**< 0.02**	0.38	48.98	< 0.01	51.24	57.10	45.10	6.66	97.80	0.01	0.29	0.15
P3	64.98	125	**< 0.02**	0.37	36.02	< 0.01	108	26.10	47.10	4.41	54.10	0.01	0.19	0.15
P4	15.13	< 0.06	**< 0.02**	< 0.03	< 0.01	< 0.01	84.18	14.20	21.70	1.73	19.80	0.01	0.25	0.21
P5	38.55	80.66	**< 0.02**	0.30	11.04	0.95	101	28.00	37.70	5.99	26.60	0.01	0.18	0.15
P6	33.33	66.29	**< 0.02**	0.20	5.77	0.12	117	26.30	35.20	4.67	27.20	0.01	0.18	0.15
P7	78.24	206	**< 0.02**	0.47	34.90	1.24	149	47.80	65.90	10.90	47.20	0.02	0.25	0.15
P8	91.97	228	**< 0.02**	0.34	12.08	0.77	150	48.70	73.50	12.60	26.80	0.01	0.26	0.16
P9	58.7	64.85	**< 0.02**	0.54	13.47	0.19	175	43.40	32.70	1.75	28.00	0.01	0.24	0.15

P10	75.11	83.92	< **0.02**	0.49	41.01	< 0.01	126	50.00	37.30	0.50	62.90	0.01	0.27	0.15
P16	61.31	119	< **0.02**	1.46	12.1	< 0.01	241	62.90	66.20	4.54	77.00	0.03	0.31	0.15
P12	690	**925**	< **0.02**	1.32	43.93	< 0.01	580	308	278	6.15	80.30	0.2	0.76	0.16
P13	55.08	44.44	< **0.02**	0.87	8.97	< 0.01	215	52.00	55.30	4.08	27.20	0.02	0.26	0.15
P14	71.53	103	< **0.02**	0.91	14.14	0.14	98.21	65.00	55.80	3.03	44.20	0.03	0.30	0.15
C2	54.85	79.4	< **0.02**	< 0.03	15.67	< 0.01	142	24.20	49.90	7.19	27.90	0.01	0.18	0.15
C3	53.9	36.7	< **0.02**	0.57	11.69	0.10	193	33.2	33.20	1.81	33.50	0.01	0.23	0.15

P=Private borehole; C=Communal borehole; S=Primary School borehole water Sample

Appendix Table 4.4: Trace Metal Concentrations in Dry Season in µg/L

	Li (Lithium)	**Be (Beryllium)**	Ti (Titanium)	V (Vanadium)	Cr (Chromium)	Mn (Manganese)	Co (Cobalt)	Ni (Nickel)	Cu (Copper)	Zn (Zinc)	**As (Arsenic)**	Cd (Cadmium)	Sb (Antimony)	2Hg (Mercury)	Pb (Lead)	U (Uranium)
S1	4.45	**< 0.06**	3.35	16.82	35.33	58.10	0.72	20.32	2.55	20.50	**< 3.38**	< 0.03	0.14	2.14	0.38	6.66
S2	4.35	**< 0.06**	3.02	24.49	37.21	39.23	0.62	20.74	1.94	32.14	**< 3.38**	< 0.03	0.11	1.76	0.32	3.56
S3	5.15	**< 0.06**	2.84	16.01	34.44	23.01	0.56	18.61	1.45	15.63	**< 3.38**	< 0.03	0.20	2.46	0.22	3.95
S4	15.91	**< 0.06**	3.04	11.88	38.98	16.91	0.45	20.79	1.02	21.75	**< 3.38**	< 0.03	< 0.04	1.68	0.14	4.75
S5	16.72	**< 0.06**	3.56	7.75	38.42	11.46	0.45	21.18	1.04	16.75	**< 3.38**	< 0.03	0.14	1.87	0.20	2.76
S6	24.82	**< 0.06**	3.33	7.12	35.31	8.81	0.44	21.36	2.09	24.77	**< 3.38**	< 0.03	< 0.04	1.50	0.21	2.59
S7	10.99	**< 0.06**	2.34	9.64	37.23	5.94	0.33	20.50	5.04	24.07	**< 3.38**	< 0.03	< 0.04	1.48	0.10	1.51
S8	6.87	**0.03**	2.57	7.67	38.44	2.99	0.36	20.52	5.67	34.66	**< 3.00**	< 0.09	0.05	2.23	1.08	1.57
S9	6.37	**0.01**	1.73	8.00	31.07	2.32	0.34	18.29	3.03	24.69	**< 3.00**	< 0.09	0.08	1.93	0.65	5.02
S10	6.26	**< 0.01**	1.92	6.29	34.99	2.34	0.32	20.22	1.33	17.47	**< 3.00**	< 0.09	< 0.02	1.72	0.24	1.33
S11	4.89	**0.05**	2.69	5.01	37.22	3.29	0.38	27.50	1.06	18.07	**< 3.00**	< 0.09	< 0.02	1.66	0.16	1.55
S12	3.43	**< 0.01**	4.09	10.10	53.33	2.07	0.30	19.97	1.21	26.17	**< 3.00**	< 0.09	0.03	1.59	0.23	1.19
S13	4.18	**0.02**	2.72	9.64	36.42	3.00	0.34	20.36	4.53	39.16	**< 3.00**	< 0.09	0.04	1.57	1.08	1.30
S14	8.53	**< 0.01**	2.84	6.78	35.77	3.56	0.40	28.15	3.12	37.60	**< 3.00**	< 0.09	< 0.02	1.62	0.46	0.32
S15	6.15	**0.02**	3.25	6.69	34.13	2.52	0.38	20.40	2.24	20.92	**< 3.00**	< 0.09	0.15	1.59	0.43	0.27
S16	5.20	**0.01**	2.92	11.53	36.68	1.77	0.34	17.64	2.24	27.28	**< 3.00**	< 0.09	< 0.02	1.48	0.43	0.33
S17	8.53	**0.01**	3.90	12.39	34.90	1.80	0.39	19.57	6.04	28.29	**< 3.00**	< 0.09	< 0.02	1.49	0.38	0.47

S19	11.33	< **0.01**	3.55	9.30	32.44	7.39	0.46	20.97	2.74	26.57	< **3.00**	< 0.09	0.05	1.51	0.98	0.13
S20	9.92	< **0.01**	2.33	6.60	34.11	2.38	0.38	32.66	2.56	68.90	< **3.00**	< 0.09	< 0.02	1.47	0.53	0.21
P1	0.96	< **0.01**	0.94	1.40	33.21	2.82	0.33	20.48	2.28	21.72	< **3.00**	< 0.09	0.10	1.47	0.24	0.14
P2	10.91	**0.04**	3.61	5.33	28.30	3.36	0.36	18.88	1.90	26.05	< **3.00**	< 0.09	< 0.02	1.45	0.37	0.15
P3	7.94	**0.04**	3.28	5.50	33.37	2.80	0.31	19.69	1.21	25.05	< **3.00**	< 0.09	< 0.02	1.45	0.28	0.97
P4	8.75	**0.01**	2.70	8.88	36.50	6.02	0.46	21.89	3.00	33.48	< **3.00**	< 0.09	0.03	1.45	0.70	1.00
P5	8.86	**0.05**	2.93	9.49	33.16	5.42	0.50	19.62	5.52	36.53	< **3.00**	< 0.09	0.03	1.44	1.56	1.12
P6	20.17	**0.09**	1.99	4.83	28.07	3.64	0.36	25.77	22.70	95.96	< **3.00**	< 0.09	0.04	1.85	0.41	3.62
P7	19.48	**0.05**	3.60	5.67	31.76	2.80	0.40	27.19	3.20	22.78	< **3.00**	< 0.09	0.03	1.52	0.38	1.40
P8	13.43	**0.09**	3.20	12.13	32.21	8.17	0.44	22.07	5.58	63.41	< **3.00**	< 0.09	< 0.02	1.50	0.98	5.69
P9	4.38	**0.02**	2.53	6.93	33.72	21.65	0.83	35.45	7.99	99.80	< **3.00**	< 0.09	0.04	1.48	1.73	1.05
P10	5.26	**0.04**	3.35	10.32	30.94	16.72	0.71	19.06	21.13	48.66	< **3.00**	< 0.09	0.10	1.45	1.70	2.59
P11	8.18	**0.02**	3.13	9.07	32.30	11.84	1.08	21.95	5.40	24.41	< **3.00**	< 0.09	0.24	2.16	0.69	17.93
P12	3.87	**0.01**	3.34	11.96	38.76	14.44	0.65	27.49	5.73	71.30	< **3.00**	< 0.09	0.04	1.49	1.53	1.96
P13	4.70	**0.01**	2.81	8.88	32.11	4.54	0.44	19.64	5.03	31.30	< **3.00**	< 0.09	< 0.02	1.45	0.62	2.34
P14	4.00	**0.01**	2.98	10.47	34.55	3.11	0.47	21.21	3.24	23.26	< **3.00**	< 0.09	0.21	1.44	0.80	2.43
P15	12.65	**0.05**	3.53	12.69	31.19	3.82	0.41	20.66	5.69	28.73	< **3.00**	< 0.09	0.04	1.44	0.46	4.62
C1	12.67	< **0.01**	3.62	9.70	33.30	5.10	0.36	20.51	3.60	36.82	< **3.00**	< 0.09	< 0.02	1.41	0.37	0.40
C2	12.57	**0.01**	2.79	8.33	31.39	25.46	0.53	20.70	2.16	25.42	< **3.00**	< 0.09	< 0.02	1.40	0.41	4.11
C3	4.32	**0.02**	2.33	14.46	37.01	4.81	0.43	19.63	1.85	17.42	< **3.00**	< 0.09	< 0.02	1.41	0.28	7.06

Appendix Table 4.5: **Trace Metal Concentration in Wet Season in mg/L**

Sample ID	Li (Lithium)	**Be (Beryllium)**	Ti (Titanium)	V (Vanadium)	Cr (Chromium)	Mn (Manganese)	Co (Cobalt)	Ni (Nickel)	Cu (Copper)	Zn (Zinc)	**As (Arsenic)**	Cd (Cadmium)	Sb (Antimony)	2Hg (Mercury)	Pb (Lead)	U (Uranium)
S1	3.93	**0.01**	3.23	23.59	35.95	3.29	0.45	19.88	1.41	24.54	**< 3.00**	< 0.09	< 0.02	1.42	0.25	4.29
S2	4.39	**0.03**	2.88	14.65	36.04	3.30	0.44	19.63	1.69	15.39	**< 3.00**	< 0.09	< 0.02	1.41	0.36	3.61
S3	11.97	**0.03**	2.96	8.71	48.71	3.54	0.46	309	33.27	50.46	**< 3.00**	< 0.09	< 0.02	1.43	0.90	4.47
S4	13.53	**0.03**	3.63	7.00	36.76	3.05	0.37	32.48	4.52	21.71	**< 3.00**	< 0.09	< 0.02	1.43	0.82	2.86
S5	23.07	**0.02**	2.83	6.44	36.78	2.65	0.42	27.50	2.06	18.46	**< 3.00**	< 0.09	0.18	1.42	0.24	2.76
S6	9.44	**0.03**	3.40	9.75	34.25	3.92	0.30	23.48	4.66	22.42	**< 3.00**	< 0.09	0.07	1.66	0.32	1.60
S7	7.31	**< 0.01**	3.30	7.53	38.07	2.15	0.34	21.13	3.19	14.55	**< 3.00**	< 0.09	< 0.02	1.42	0.15	1.83
S8	5.74	**0.02**	3.34	7.76	34.89	2.54	0.39	23.77	4.66	19.96	**< 3.00**	< 0.09	< 0.02	1.44	0.65	5.08
S9	6.17	**< 0.01**	2.36	5.85	32.38	11.92	0.32	19.89	2.79	24.24	**< 3.00**	< 0.09	< 0.02	1.40	0.27	1.59
S10	4.85	**0.02**	2.61	5.59	35.10	2.66	0.34	22.30	1.81	20.12	**< 3.00**	< 0.09	< 0.02	1.38	0.48	1.81
S11	2.85	**0.01**	4.17	9.16	49.05	8.90	0.29	19.00	1.15	15.21	**< 3.00**	< 0.09	< 0.02	1.39	0.58	1.32
S12	3.81	**0.02**	2.89	8.41	37.90	2.79	0.38	20.01	6.09	17.66	**< 3.00**	< 0.09	0.04	1.41	0.40	1.47
S13	6.21	**< 0.01**	2.55	11.27	32.24	2.69	0.37	19.09	2.93	59.59	**< 3.00**	< 0.09	< 0.02	1.41	0.35	1.11
S14	7.20	**< 0.01**	4.82	8.17	36.44	26.51	0.45	22.06	4.67	21.88	**< 2.00**	< 0.01	< 0.06	1.25	0.37	0.24
S15	6.42	**< 0.01**	5.20	17.85	55.83	17.67	0.54	26.36	2.17	33.54	**< 2.00**	< 0.01	< 0.06	1.28	0.19	0.41
S16	13.36	**< 0.01**	5.24	17.74	50.85	15.52	0.63	27.57	1.76	23.25	**< 2.00**	< 0.01	< 0.06	1.18	0.22	0.64
S17	16.93	**< 0.01**	6.33	21.38	68.73	17.46	0.78	36.59	4.54	19.48	**< 2.00**	< 0.01	< 0.06	1.21	0.25	1.07
S18	20.64	**0.04**	5.87	13.93	61.20	9.22	0.73	37.16	2.66	40.35	**< 2.00**	0.02	< 0.06	1.24	0.44	0.22
S19	14.14	**0.03**	5.61	10.11	48.02	7.20	0.66	46.05	2.77	42.97	**< 2.00**	0.02	0.17	1.14	0.81	0.30
S20	22.01	**< 0.01**	6.27	15.41	52.71	5.82	0.57	32.01	58.58	52.50	**< 2.00**	< 0.01	0.10	1.15	2.87	0.38

P1	42.00	**0.06**	4.67	6.03	44.72	5.40	0.63	29.40	15.19	94.52	< **2.00**	0.04	0.10	1.12	2.78	1.83
P2	18.61	**0.03**	5.98	8.16	47.42	3.93	0.61	26.17	2.63	21.36	< **2.00**	< 0.03	< 0.06	1.09	0.55	0.25
P3	8.07	**0.10**	2.51	5.00	27.56	2.05	0.24	16.35	3.80	24.44	< **3.00**	< 0.03	< 0.02	1.39	0.67	1.13
P4	8.59	< **0.05**	2.29	8.85	27.46	2.24	0.37	16.84	17.85	29.77	< **3.00**	< 0.03	< 0.02	1.39	1.37	1.25
P5	7.96	< **0.01**	2.06	8.07	32.07	1.63	0.28	16.93	7.38	20.86	< **2.00**	< 0.01	< 0.08	2.88	0.32	0.91
P6	22.24	**0.13**	1.38	3.93	28.61	2.52	0.39	22.64	3.09	18.52	< **2.00**	< 0.01	< 0.08	2.54	0.21	0.03
P7	19.30	**0.07**	1.94	4.94	34.60	2.53	0.41	25.16	19.56	24.46	< **2.00**	< 0.01	< 0.08	2.42	0.93	0.03
P8	5.16	< **0.01**	2.48	7.03	31.92	5.82	0.52	19.55	11.23	110.20	< **2.00**	0.02	< 0.08	2.35	0.98	0.03
P9	5.38	**0.03**	1.09	13.81	34.48	4.33	0.43	19.82	2.65	19.92	< **2.00**	< 0.01	< 0.08	2.29	0.38	0.03
P10	9.19	**0.18**	25.38	11.08	64.61	16.54	1.57	25.89	8.60	21.05	< **2.00**	0.02	< 0.08	5.43	4.14	0.03
C2	13.17	< **0.01**	4.87	24.53	72.84	20.27	0.85	40.21	20.35	54.82	< **2.00**	0.05	0.06	1.19	3.28	0.97
C3	1.19	**0.03**	1.28	0.42	31.94	17.17	0.57	20.99	5.55	35.92	< **3.00**	< 0.09	< 0.02	1.41	0.33	0.38

Appendix Table 4.6: Analytical results of physico-chemical parameters throughout the study**.**

Sample Code	Salinity	Salinity	Salinity	pH Aug	pH Oct	pH Nov	EC (µS/cm)	EC (µS/cm)	EC (µS/cm)	TDS (mg/L)	TDS (mg/L)	TDS (mg/L)	Temp (°C)	Temp (°C)	Temp (°C)	Turbidity	Turbidity	Turbidity
S1	485.0	430.0	387.0	7.4	8.0	7.8	924.0	941.3	1020.	600.6	611.8	663.2	25.0	26.5	25.8	0.0	0.0	0.0
S2	661.0	593.0	492.0	7.8	7.7	7.7	1202.	680.0	1125.	781.3	442.0	731.5	25.5	26.5	26.0	0.0	0.0	0.0
S3	202.0	348.0	385.0	7.4		7.4	449.9		756.7	292.4		491.8	24.2		23.0	0.0	0.0	0.0
S4	296.0	325.0	326.0	7.5	7.4	7.4	617.0	544.5	683.0	401.1	353.9	444.0	23.8	31.3	27.6	0.0	0.0	0.0
S5	278.0	311.0	301.0	7.2		7.3	581.0		618.7	377.7		402.1	24.3		12.2	0.0	0.0	0.0
S6	597.0	405.0	338.0	7.1	7.0	7.6	781.0	872.0	723.3	507.7	566.8	470.2	24.0	30.1	27.1	0.0	0.0	0.0
S7	188.0	176.0	191.0	7.2	7.2	7.2	417.7	242.5	446.1	271.5	157.6	290.0	24.9	30.4	27.7	0.0	0.0	0.0
S8	371.0	247.0	246.0	7.1	7.1	7.2	472.2	562.5	491.5	306.9	365.6	319.5	24.5	30.7	27.6	0.0	0.0	0.0
S9	328.0	307.0	228.0	7.4	7.4	7.7	617.0	710.0	653.0	401.1	461.5	424.5	23.2	30.3	26.7	0.0	0.0	0.0
S10	120.0	148.0	116.0	7.2	7.2	7.1	351.4	424.8	393.6	228.4	276.1	255.8	24.5	30.5	27.5	0.0	0.0	0.0
S11	187.0	225.0	165.0	6.9	6.9	7.1	420.7	506.3	418.3	273.5	329.1	271.9	23.7	30.3	27.0	0.0	0.0	0.0
S12	298.0	257.0	193.0	7.3	7.3	7.6	388.7	448.1	430.5	252.7	291.3	279.8	24.2	30.6	27.4	0.0	0.0	0.0
S13	216.0	210.0	209.0	7.0	7.4	7.1	398.7	448.3	466.3	259.2	291.4	303.1	25.6	31.0	28.3	0.0	0.0	0.0
S14	507.0	355.0	310.0	7.2	7.2	7.5	679.0	591.9	806.7	441.4	384.8	524.3	25.2	30.6	27.9	0.0	0.0	0.0
S15	349.0	235.0	178.0	7.6	7.3	7.7	448.0	470.3	472.6	291.2	305.7	307.2	25.1	30.8	28.0	0.0	0.0	0.0
S16	209.0	278.0	175.0	7.4	7.0	7.6	519.0	547.7	575.7	337.4	356.0	374.2	24.1	31.0	27.6	0.4	0.0	0.0

S17	185.0	302.0	248.0	7.4	7.3	7.5	432.9	626.3	667.7	281.4	407.1	434.0	24.5		24.0	0.0	0.0	0.0
S18	254.0	277.0	281.0	7.1	8.1	8.0	566.0	581.3	617.7	367.9	377.8	401.5	24.0	26.6	25.3	0.3	0.0	0.0
S19	330.0	286.0	337.0	7.3	7.2	7.2	688.0	713.5	704.3	447.2	463.8	457.8	27.9	26.7	27.3	0.0	0.0	0.0
S20		315.0	293.0	-	6.8	6.8	-	838.0	631.7		544.7	410.6	-	26.7	23.0	-	0.0	0.0
S21	-	200.0	-	-	8.4		-	484.6			315.0	299.4	-	31.0	24.0	-	0.0	0.0
P1	310.6	348.1	340.0	7.1	7.2	7.5	647.0	725.3	460.7	420.6	471.4	744.9	23.3	26.4	24.8	0.0	0.0	0.0
P2	126.8		514.0	8.3		7.2	264.1		1146.	171.7	0.0	744.9	24.2		12.1	0.0	0.0	0.0
P3	331.2	360.5	234.0	7.2	7.1	7.3	690.0	751.0	812.0	448.5	488.2	527.8	24.6	26.7	25.6	0.4	0.0	0.0
P4	175.5	172.7	181.0	6.9	7.1	**10.9**	365.7	359.8	385.5	237.7	233.9	250.6	23.9	26.8	25.4	0.0	0.0	0.0
P5	259.2	307.5	278.0	7.2	7.2	7.3	540.0	640.7		351.0	416.4	0.0	24.0	31.5	27.8	0.0	0.0	0.0
P6	265.4	283.3	255.0	7.3	7.1	7.0	553.0	590.3	495.2	359.5	383.7	321.9	24.5	31.0	27.8	0.0	0.0	0.0
P7	478.6	514.7	488.0	7.1	7.1	6.9	997.0	1072.	916.0	648.1	697.0	595.4	23.4	31.0	27.2	0.0	0.0	0.0
P8	465.6	499.3	490.0	7.1	7.2	7.6	970.0	1040.	766.3	630.5	676.2	498.1	25.6	30.9	28.2	0.0	0.0	0.0
P9	299.0	163.3	307.0	7.3	7.5	7.3	623.0	340.3	781.3	405.0	221.2	507.9	23.1	31.2	27.2	0.1	0.0	0.0
P10	348.5	393.6	383.0	6.9	7.3	7.3	726.0	820.0	619.7	471.9	533.0	402.8	24.3	31.0	27.7	0.0	0.0	0.0
P11	487.2			7.6			1015.			659.8			25.6			0.0	0.0	0.0
P12	1932.	2111.	288.0	6.8	7.0		4025.	4398.		2616.	2858.	0.0	25.4	31.1	28.3	0.0	0.0	0.0
P13	345.1	391.5	371.0	7.2	7.5	8.0	719.0	815.7	764.0	467.4	530.2	496.6	25.2	31.1	28.2	0.0	0.0	0.0
P14	408.0	464.0	378.0	7.2	7.3	7.6	850.0	966.7	778.5	552.5	628.3	506.0	25.6	31.2	28.4	0.0	0.0	0.0
P15	447.8	535.7	–	7.7	7.9		933.0	1116.	–	606.5	725.4	–	25.6	31.2	28.4	0.0	0.0	0.0
C1	230.0	233.8		7.9	7.9		479.1	487.0		311.4	316.6		26.8	30.7		0.0	0.0	0.0
C2	301.4	325.0	294.0	6.9	7.2	7.0	628.0	677.0	720.5	408.2	440.1	468.3	23.5	26.6	25.0	0.3	0.1	0.0

C3	279.4	0.0	303.0	7.0	7.3	582.0	517.3	378.3	0.0	336.2	23.6	22.0	0.9	0.0	0.0	

Appendix Table 4.7. The set standard guideline values of water quality for drinking water by the Republic of South Africa and World Health Organisation.

Parameter	**DWAF 1996**	**WHO Values**	**SANS 2006**	**SANS**
V			200	
Cr	50 (Total)	50[#]	100 (Total)	50
Mn	50	100[#]		400
Co (Cobalt)			500	500
Ni (Nickel)	-	500[*]		70
Cu (Copper)	1000	2000[*#]		2000
Zn (Zinc)	3000	3000[*], 10[#]		5000
As (Arsenic)		10[#]		
(Selenium)				40
Cd	5	3[*#]		3
Sb				20
Hg (Mercury)				6
Pb (Lead)	10	10[*#]		10
U (Uranium)				30

Source: [*] WHO (1993), [#] WHO (2004). pH has no unit

Appendix Table 4.8: The detected mean levels of microbial parameters in Collins Chabane and Makhado Municipality.

Sample Code	*E. Coli* (Cfu/100mL) Aug	*E. Coli* (Cfu/100mL) Oct	*E. Coli* (Cfu/100mL) Nov	Total Coliform Aug	Total Coliform Oct	Total Coliform Nov
S1	0	0	0	2	16	103
S2	0	0	0	132	82	504
S3	0	3	0	83	504	61
S4	0	0	0	49	21	302
S5	0	0	0	28	231	56.5
S6	0	1	0	55	44	500
S7	0	0	0		97	222
S8	0	2	0	82	99	
S9	0	0	0	66	178	268
S10	15	0	0	61	247	241
S11	8	0	0	42	37	
S12	65	25	190	71	150	490
S13		0	0		31	40
S14	0	0	0	37	36	350
S15	0	23	0	17	174	895
S16	1	11	0	22	143	29
S17	0	0	N	25	135	
S18	10	0	0		3	14
S19	0	0	0	120	32	83
S20	-	0	0		10	
S21	-					
P1	0	0	0		3	0
P2	0			28		161
P3	0	0		0	15	
P4		0			120	
P5		0	0	0	66	275
P6		0	0	0	140	151.5
P7	0	0	0	32	39	77
P8	0		0	3		11
P9	0	0	0	85	400	610
P10		0	0	0	74	42
P11	0			140		
P12	0	0	0	35	40	
P13	76	28	0	87.5	90	4
P14	0		0	1280		960
P15	0		–	0		
C1	2	0		53	22	
C2	2	0	0	2	59	19
C3	1	-	0	224	-	0

Appendix Table 5.1: The average values of non-carcinogenic health risk assessment for selected heavy metals in groundwater samples from school's borehole in dry season

	Ding (Child)	**Ding (Adult)**	**HQing (Child)**	**HQing (Adult)**	**CDIing (Child)**	**CDIing (Adult)**	**Dderm (Child)**	**Dderm (Adult)**	**HQderm (Child)**	**HQderm (Adult)**	**HQing/ HQderm_Child**	**HQing/ HQderm_Adult**
Fe	**1.0E-06**	**6.0E-04**	1.2E-01	2.3E+06	2.3E-03	6.0E-04	8.4E-06	2.6E-10	1.0E+08	3.3E+12	4.5E-14	8.6E-07
V	**5.4E-04**	**3.2E-01**	1.2E-01	2.3E+06	2.4E-01	6.4E-02	4.5E-03	1.4E-07	1.3E+03	4.2E+07		
Cr	**4.4E+00**	**1.2E+00**	1.4E+02	6.1E+01	4.4E+00	1.2E+00	3.2E-02	1.9E-02	9.4E+01	1.6E+02	8.6E-01	3.8E-01
Mn	**5.3E+00**	**1.4E+00**	2.7E+02	1.2E+02	5.3E+00	1.4E+00	1.9E-02	1.1E-02	1.4E+03	2.3E+03	1.3E-01	5.8E-02
Co	**5.0E-02**	**1.3E-02**	2.7E+01	1.2E+01	5.0E-02	1.3E-02	1.8E-03	1.1E-03	1.1E+04	2.0E+04	1.5E-03	6.6E-04
Ni	**2.6E+00**	**6.8E-01**	2.7E+02	1.2E+02	2.6E+00	6.8E-01	9.5E-03	5.5E-03	7.5E+04	1.3E+05	7.6E-02	3.4E-02
Cu	**3.2E-01**	**8.4E-02**	2.7E+02	1.2E+02	3.2E-01	8.4E-02	1.2E-03	6.9E-04	4.6E+04	7.9E+04	4.7E-03	2.1E-03
Zn	**3.3E+00**	**8.7E-01**	4.5E+02	2.0E+02	3.3E+00	8.7E-01	7.3E-03	4.3E-03	4.6E+03	7.9E+03	6.5E-02	2.9E-02
Cd	**8.1E-03**	**2.1E-03**	2.7E+02	1.2E+02	8.1E-03	2.1E-03	3.0E-05	1.7E-05	2.2E+04	3.8E+04	9.5E-03	4.3E-03
Hg	**2.1E-01**	**5.4E-02**	2.7E-01	1.2E-01	2.1E-01	5.4E-02	7.6E-01	4.4E-01	4.0E-01	6.9E-01	4.0E-01	1.8E-01
Pb	**5.2E-02**	**1.4E-02**	6.8E+01	3.1E+01	5.2E-02	1.4E-02	7.6E-04	4.4E-04	2.9E+03	2.9E+03	2.2E-02	9.7E-03
Al	6.3E-03	1.7E-03	2.7E+02	1.2E+02	6.3E-03	1.7E-03	2.3E-05	1.4E-05	1.3E+08	2.3E+08		
As	3.8E-01	9.9E-02	2.7E+02	1.2E+02	3.8E-01	9.9E-02	1.4E-03	8.1E-04	2.2E+02	3.7E+02	7.3E-01	3.3E-01
										∑HI	2.30E+00	1.03E+00

Appendix Table 5.2: The average values of non-carcinogenic health risk assessment for selected heavy metals in groundwater samples from school's borehole in wet season Municipalities in wet season

	Ding (Child)	Ding (Adult)	HQing (Child)	HQing (Adult)	CDIing (Child)	CDIing (Adult)	Dderm (Child)	Dderm (Adult)	HQderm (Child)	HQderm (Adult)	HQing/HQderm Child	HQing/HQderm Adult
Fe	**8.10E-06**	**4.82E-03**	1.20E-01	2.31E+06	1.84E-02	4.82E-03	6.75E-05	2.08E-09	1.04E+07	3.36E+11	3.57E-13	6.89E-06
V	**6.08E-04**	**3.62E-01**	1.20E-01	2.31E+06	2.74E-01	7.18E-02	5.07E-03	1.56E-07	1.19E+03	3.84E+07		
Cr	**5.17E+00**	**1.35E+00**	1.36E+02	6.11E+01	5.17E+00	1.35E+00	3.79E-02	2.22E-02	8.31E+01	1.42E+02	1.01E+00	4.51E-01
Mn	**9.17E-01**	**2.40E-01**	2.73E+02	1.22E+02	9.17E-01	2.40E-01	3.36E-03	1.96E-03	1.27E+04	2.17E+04	2.23E-02	1.00E-02
Co	**5.54E-02**	**1.45E-02**	2.73E+01	1.22E+01	5.54E-02	1.45E-02	2.03E-03	1.19E-03	1.07E+04	1.83E+04	1.62E-03	7.26E-04
Ni	**4.83E+00**	**1.26E+00**	2.73E+02	1.22E+02	4.83E+00	1.26E+00	1.77E-02	1.03E-02	6.21E+04	1.06E+05	1.41E-01	6.32E-02
Cu	**8.84E-01**	**2.32E-01**	2.73E+02	1.22E+02	8.84E-01	2.32E-01	3.24E-03	1.89E-03	3.31E+04	5.66E+04	1.29E-02	5.79E-03
Zn	**3.35E+00**	**8.77E-01**	4.55E+02	2.04E+02	**3.35E+00**	**8.77E-01**	7.37E-03	4.31E-03	4.87E+03	8.33E+03	6.53E-02	2.92E-02
Cd	**7.52E-03**	**1.97E-03**	2.73E+02	1.22E+02	7.52E-03	1.97E-03	2.76E-05	1.61E-05	4.35E+04	7.44E+04	8.79E-03	3.94E-03
Hg	**1.62E-01**	**4.25E-02**	2.73E-01	1.22E-01	1.62E-01	4.25E-02	5.95E-01	3.48E-01	5.08E-01	8.70E-01	3.16E-01	1.42E-01
Pb	**6.56E-02**	**1.72E-02**	6.82E+01	3.06E+01	6.56E-02	1.72E-02	9.62E-04	5.62E-04	2.29E+03	2.29E+03	2.74E-02	1.23E-02
Al	2.38E-02	6.24E-03	2.73E+02	1.22E+02	2.38E-02	6.24E-03	8.74E-05	5.11E-05	8.30E+06	1.42E+07		
As	3.18E-01	8.33E-02	2.73E+02	1.22E+02	3.18E-01	8.33E-02	1.17E-03	6.81E-04	2.67E+02	4.57E+02	6.19E-01	2.78E-01
										∑HI	2.22E+00	9.96E-01

Appendix Table 5.3: The average values of non-carcinogenic health risk assessment for selected heavy metals in groundwater samples from household and communal boreholes in dry season

	Ding (Child)	**Ding (Adult)**	**HQing (Child)**	**HQing (Adult)**	**CDIing (Child)**	**CDIing (Adult)**	**Dderm (Child)**	**Dderm (Adult)**	**HQderm (Child)**	**HQderm (Adult)**	**HQing/HQderm_ Child**	**HQing/HQderm_ Adult**
Fe	**2.9E-06**	**1.7E-03**	1.2E-01	2.3E+06	6.6E-03	1.7E-03	2.4E-05	7.4E-10	7.4E+07	2.4E+12	1.3E-13	2.5E-06
V	**4.6E-04**	**2.7E-01**	1.2E-01	2.3E+06	2.1E-01	5.4E-02	3.8E-03	1.2E-07	1.8E+03	5.7E+07		
Cr	**3.9E+00**	**1.0E+00**	1.4E+02	6.1E+01	**3.9E+00**	**1.0E+00**	2.9E-02	1.7E-02	1.0E+02	1.8E+02	7.7E-01	3.4E-01
Mn	**9.8E-01**	**2.6E-01**	2.7E+02	1.2E+02	9.8E-01	2.6E-01	3.6E-03	2.1E-03	1.1E+04	1.9E+04	2.4E-02	1.1E-02
Co	**6.0E-02**	**1.6E-02**	2.7E+01	1.2E+01	6.0E-02	1.6E-02	2.2E-03	1.3E-03	1.0E+04	1.7E+04	1.8E-03	7.9E-04
Ni	**4.8E+00**	**1.3E+00**	2.7E+02	1.2E+02	**4.8E+00**	**1.3E+00**	1.8E-02	1.0E-02	6.4E+04	1.1E+05	1.4E-01	6.3E-02
Cu	**7.1E-01**	**1.9E-01**	2.7E+02	1.2E+02	7.1E-01	1.9E-01	2.6E-03	1.5E-03	2.7E+04	4.6E+04	1.0E-02	4.7E-03
Zn	**4.9E+00**	**1.3E+00**	4.5E+02	2.0E+02	**4.9E+00**	**1.3E+00**	1.1E-02	6.3E-03	3.6E+03	6.2E+03	9.5E-02	4.3E-02
Cd	**1.1E-02**	**2.8E-03**	2.7E+02	1.2E+02	1.1E-02	2.8E-03	4.0E-05	2.3E-05	1.3E+04	2.2E+04	1.3E-02	5.7E-03
Hg	**1.8E-01**	**4.8E-02**	2.7E-01	1.2E-01	1.8E-01	4.8E-02	6.7E-01	3.9E-01	4.6E-01	7.8E-01	3.5E-01	1.6E-01
Pb	**9.0E-02**	**2.4E-02**	6.8E+01	3.1E+01	9.0E-02	2.4E-02	1.3E-03	7.7E-04	1.6E+03	1.6E+03	3.8E-02	1.7E-02
Al	8.4E-03	2.2E-03	2.7E+02	1.2E+02	8.4E-03	2.2E-03	3.1E-05	1.8E-05	1.2E+08	2.0E+08		
As	3.6E-01	9.4E-02	2.7E+02	1.2E+02	3.6E-01	9.4E-02	1.3E-03	7.7E-04	2.3E+02	3.9E+02	7.0E-01	3.1E-01
										∑HI	2.15E+00	9.62E-01

Appendix Table 5.4: The average values of non-carcinogenic health risk assessment for selected heavy metals in groundwater samples from household and communal boreholes in wet season

	Ding (Child)	**Ding (Adult)**	**HQing (Child)**	**HQing (Adult)**	**CDIing (Child)**	**CDIing (Adult)**	**Dderm (Child)**	**Dderm (Adult)**	**HQderm (Child)**	**HQderm (Adult)**	**HQing/HQderm_ Child**	**HQing/HQderm_ Adult**
Fe	**8.32E-06**	**4.95E-03**	1.20E-01	2.31E+06	1.89E-02	4.95E-03	6.93E-05	2.14E-09	1.02E+07	3.29E+11	3.67E-13	7.08E-06
V	**4.48E-04**	**2.67E-01**	1.20E-01	2.31E+06	2.02E-01	5.29E-02	3.73E-03	1.15E-07	3.71E+03	1.20E+08		
Cr	**4.78E+00**	**1.25E+00**	1.36E+02	6.11E+01	4.78E+00	1.25E+00	3.51E-02	2.05E-02	9.43E+01	1.61E+02	9.32E-01	4.18E-01
Mn	**8.44E-01**	**2.21E-01**	2.73E+02	1.22E+02	8.44E-01	2.21E-01	3.10E-03	1.81E-03	1.52E+04	2.60E+04	2.06E-02	9.21E-03
Co	**6.88E-02**	**1.80E-02**	2.73E+01	1.22E+01	6.88E-02	1.80E-02	2.52E-03	1.47E-03	1.00E+04	1.71E+04	2.01E-03	9.01E-04
Ni	**2.80E+00**	**7.33E-01**	2.73E+02	1.22E+02	2.80E+00	7.33E-01	1.03E-02	6.00E-03	7.27E+04	1.24E+05	8.18E-02	3.67E-02
Cu	**1.18E+00**	**3.09E-01**	2.73E+02	1.22E+02	1.18E+00	3.09E-01	4.32E-03	2.53E-03	1.58E+04	2.71E+04	1.72E-02	7.72E-03
Zn	**4.76E+00**	**1.25E+00**	4.55E+02	2.04E+02	**4.76E+00**	**1.25E+00**	1.05E-02	6.12E-03	4.05E+03	6.93E+03	9.27E-02	4.15E-02
Cd	**3.48E-03**	**9.12E-04**	2.73E+02	1.22E+02	3.48E-03	9.12E-04	1.28E-05	7.46E-06	6.23E+04	1.07E+05	4.07E-03	1.82E-03
Hg	**2.55E-01**	**6.68E-02**	2.73E-01	1.22E-01	2.55E-01	6.68E-02	9.35E-01	5.46E-01	3.98E-01	6.81E-01	4.97E-01	2.23E-01
Pb	**1.59E-01**	**4.17E-02**	6.82E+01	3.06E+01	1.59E-01	4.17E-02	2.34E-03	1.37E-03	1.37E+03	1.37E+03	6.65E-02	2.98E-02
Al	2.76E-02	7.23E-03	2.73E+02	1.22E+02	2.76E-02	7.23E-03	1.01E-04	5.91E-05	7.11E+06	1.22E+07		
As	2.70E-01	7.07E-02	2.73E+02	1.22E+02	2.70E-01	7.07E-02	9.90E-04	5.79E-04	3.13E+02	5.35E+02	5.26E-01	2.36E-01
										∑HI	2.24E+00	1.00E+00