Assessment of minor ions and trace element chemistry in groundwater in Luvuvhu catchment, Limpopo province, South Africa

BY

Madondo Takalani Patience (200711984)

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Supervisor

Prof. Vetrimurugan Elumalai

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DECLARATION

I, Ms. Madondo Takalani Patience declare that the thesis titled "Assessment of minor ions and trace element chemistry in groundwater in Luvuvhu catchment, Limpopo province, South Africa" submitted in fulfilment of the degree of Master of Science (specialising in Hydrology) is my original work duly performed in the Faculty of Science, Agriculture and Engineering at the University of Zululand. This work has not been submitted before by anyone from University of Zululand or any other institution and all the sources I have used have been acknowledged by complete references.

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APPROVAL:

Supervisor: Prof. V. Elumalai……………………….. Date: 17.03.2022

Mr. Brian K Rawlins……………………………………… Date: 17.03.2022

CONTRIBUTION TO THE BODY OF KNOWLEDGE

The results from this research have been published in peer-reviewed journals and presented an article at international conference of which the papers are attached in the APPENDIX:

Article:

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ABSTRACT

Agricultural activities are often associated with contamination of water, which resulted in high concentration of nutrients and trace metals in the shallow aquifer. Occurrence and distribution of nutrients and trace metals in the groundwater of intensively irrigated region of Luvuvhu catchment was carried out to determine the status of groundwater quality and its suitability for drinking. Groundwater samples were collected and analysed for physiochemical parameters. The results suggest that the concentration of nutrients and trace metals in the groundwater are below the permissible limit of drinking water standards recommended by the World Health Organization and South African standards except pH, K and Pb. Low pH (51%), potassium (31%) and lead (100%) restrict the groundwater usage for drinking. Relation between groundwater flow direction and EC, sulphate, nitrate, and ammonium contents indicate that it is mostly constant towards the centre of the study area, but sudden enrichment is noticed in the downstream. Silica and fluoride has increased along with the direction of groundwater flow. Trace metals (B, Pb and Zn) show decreasing trend in the flow direction. However, pH, K, Li, Cr, and phosphate concentrations do not show significant variation along the flow direction. Positive relation between nitrate, EC, sulphate, and ammonium implies that groundwater quality is affected by the surface contamination sources, and mostly from irrigation return flow, through the application of fertilizers and organic manures. However, groundwater with high silica and fluoride also has high nitrate, which justifies that wastewater infiltration from the surface has triggered the mineral dissolution in the vadose. Trace metals does not correlate with nitrate. High concentrations of trace metals are recorded with low nitrate, which implies that metals are derived from mineral weathering. However, boron concentrations in a few wells show positive

relation with nitrate, which justified the impact of natural sources and irrigational activities.

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List of abbreviations

B	Boron
Cl^-	Chloride ion
MAP	Mean Annual Precipitation
DDT	Dichlorodiphenyltrichloroethane
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
DWS	Department of Water and Sanitation
DWS ISP	Department of water and sanitation internal strategic perspective
EC	Electrical Conductivity
Fe	Iron
GPS	Global Positioning System
GIS	Geographic Information System
ICP-OES	Inductive Coupled Plasma Optical Emission Spectrophotometer
MCL	Maximum contaminant level
meq/l	Milli equivalents per Litre
Mg^{2+}	Magnesium ion
mg/l	Milligrams per Litre
mS/m	MilliSiemens per meter
Na^+	Sodium ion
NEER	Engineering research institute, India
NO_3^-	Nitrate ion
NWRS	National Water Resource Strategy
SANS	South African National Standards

SAWS	South African weather service
SO_4^{2-}	Sulphate ion
TDS	Total Dissolved Solids
TH	Total Hardness
WHO	World Health Organization
WMA	Water Management Area
UNESCO	United nations educational scientific and cultural organisation

1. Chapter one

1. Introduction:

Water is an essential element of our daily lives; it is also very essential for the entire ecosystem (Tiwari et al., 2013). About seventy percent of the earth's surface is covered with water. Only one percent of freshwater is flowing through rivers, lakes, and underground streams (SDWF, 2015). Groundwater is normally defined as the water found underground in the cracks and spaces in soil, sand, and rock. It is stored and moves slowly through geologic formations of soil, sand, and rocks (DWA, 2010). Approximately, two third of South Africa's population depends on groundwater for their domestic use (Water research commission, 2015). In over 90% of the surface of South Africa, groundwater occurs in hard rock with no pore spaces (DWA, 2010).

For many years groundwater has always been considered as the major source of freshwater reservoirs. Groundwater provides water for different and important human and ecological needs such as human consumption, agriculture, industry, and many groundwater-dependent ecosystems, especially during droughts (Klove et al., 2014). Groundwater is the primary source of drinking water for more than 1.5 billion people worldwide. Studies conducted by the Department of water affairs suggest that South Africa's groundwater resources supplies approximately 15% of the total volume of water consumed nationally and almost 64% is used for irrigation while exploration mining and domestic consumption constitutes 8% (DWAF, 2002). Groundwater has always been considered a major source of freshwater reservoirs and it provides water for different human needs such as drinking, domestic, agriculture and industrial usage (Vetrimurugan and Elango 2014; Agca et al. 2014; Barzegar et al. 2017; Chidambaram et al. 2018; Heydarirad et al. 2019; Zhou et al. 2020). Water availability, accessibility and quality become more complicated worldwide in recent days due to climate change, natural and manmade activities. The groundwater chemistry is largely influenced by various natural and anthropogenic factors. Natural factors namely temperature, pressure, rock types, soil formations, residence time, infiltration rate, etc. determines the water chemistry and quality (DWA 2010; Atikul et al. 2016; Magesh et al. 2017; Mthembu et al. 2020; Busico et al. 2017; Lwimbo et al. 2019; Kumar and Singh 2020; Rakib et al. 2020). Besides, the impact of human activities other environmental parameters may also affect the geochemical mobility of certain constituents in groundwater (Chenini and Khmiri 2009).

About 74% of South Africans living in rural communities depends entirely on groundwater and 14% partially depends on groundwater for domestic use (UNESCO, 2006). In Limpopo province alone the people depending on groundwater for domestic use are 70% (Water S.A, 2012). This makes the study on groundwater chemistry very important as many groundwater resources are non-renewable on meaningful time scales for both human society and ecosystem (Klove et al., 2014).

According to a study conducted by the Department of Water affairs groundwater is contained in faults, fractures, and joints and in dolomite limestone (DWA, 2010). When water is moving downwards its mineral matter is altered by effects of geological processes naturally. Groundwater contains mineral ions which have slowly dissolved from the environment around it. These mineral ions are from soil particles, sediments, and rocks which dissolve and mixes with water flowing as it travels along mineral surfaces in the pores or fractures of the unsaturated zone of the aquifer (Harter, 2003). The dissolved ions in groundwater are known as total dissolved solids (TDS).Total dissolved solids in water are divided into three groups: major constituents, minor constituents, and trace elements (Harter, 2003). Minor ions are said to be the constituents with concentration of 0.01-10 mg/l and trace elements are trace constituents that are present in concentration lower than 0.1 mg/l in water (Domenico and Schwartz, 1990). In many areas trace elements occurs in small concentration that they are considered not a threat in human health. Many of the trace elements are said to be essential for the human metabolism (Harter, 2003). However, in some instances trace elements occur in high concentration that makes water to be unsuitable for drinking e.g., chromium and arsenic for industrial activities (Edet et al., 2014).

Groundwater has become the most dependable source in Luvuvhu catchment especially downstream of Albasin dam. The dam can no longer yield sufficient volumes to meet the required agricultural volume for the Luvuvhu government water scheme and new emerging farmers. Farmers are opting to using groundwater to supplement the shortage in water supply. Rural domestic supply is also another large-scale user of groundwater especially in Thohoyandou town and the surrounding rural areas. Other uses of groundwater in Luvuvhu catchment is stock watering. The groundwater used in the study area is not monitored and there is no certainty on impact of over-utilization of the resource (DWAF, 2004).According to the NWRS (2004) the quality and quantity of groundwater from Luvuvhu sub-catchment is not known. Groundwater quality is of major importance as it impacts on human and ecological health; therefore, it is indeed of greater importance to assess the chemistry of groundwater by analysing the minor ions and trace element composition.

1.1 Groundwater Quality

Groundwater quality is very dependent on the type of rock, formations of the soil through which it flows. It is also dependent on the residence time and temperature and pressure conditions. The quality of groundwater in different places differs depending on the aquifer in which it is found. In South Africa water from Limpopo province in granites contains high concentrations of fluoride. Soil also has an impact on the chemistry of groundwater. Soil contains carbon dioxide in high concentration, and the carbon dioxide dissolves in water. Dissolved carbon dioxide creates a weak acid which in turn can dissolve many silicate minerals (GSSA, 2016). Trace metal concentrations in groundwater has been one of the important concern, high concentrations of trace elements have been found in groundwater (Smith et al., 2000; Armah et al., 2014).

Trace metals can occur due to anthropogenic activities, of which agricultural land uses, is one of the causes. Irrigation uses animal manure, fertilizers and pesticides which can have an impact on groundwater quality. Mining processes such as metal finishing and smelting can also increase the concentration of trace metals in ground water. Sewage sludge, waste from landfills petrol stored underground can also increase the concentration of trace metals (Adriano, 2001). The world health organisation has reported that cases recorded of human poisoning due to diseases related to polluted water caused approximately five million deaths (WHO, 1995).

1.2 Groundwater pollution

Groundwater is normally perceived as clean water and naturally fit for domestic use; it is also less vulnerable to pollution due to the unsaturated zone that protects it from pollution. Varol and Sen define water pollution as direct and indirect introduction of pollutants that can harm living organisms (Varol and Sen, 2012). Pollution of groundwater can come from various sources and it can make water to be unfit for human consumption and other domestic uses. Polluted groundwater is difficult and expensive to treat (DWA, 2010).

One of the biggest sources of groundwater contamination in Southern Africa is agriculture because of the use of pesticides, herbicides, and fertilizers. Over the past 20 to 30 years farmers have relied on the use of agricultural chemicals to increase production; however, this has had an adverse impact on the quality of ground water in many major agricultural areas of the world. Pollution of ground water, associated to nitrogen fertilizers and pesticides, repetitive land application, as well as point sources is increasing at an alarming rate and it is becoming a serious problem (Hallberg,1987).

Fertilizers that are used in irrigation contain inorganic nitrates from potassium nitrate and ammonium nitrate containing fertilizers. Inorganic nitrates can be dangerous to health of human beings if consumed in high concentrations. High concentration of inorganic nitrate is mostly harmful to the health of elderly, young children, and people with immune compromised systems. The study show that in South Africa about 25% of boreholes in Limpopo province particularly in areas around Mokopane and Soutpansberg are high in fluoride and nitrate concentrations.(Tredoux and Talma, 2006).

1.3 Groundwater chemical composition

Water is regarded as a good medium for chemical reaction processes and it influences geochemical activities that control groundwater chemistry (Smedley and Kinniburgh, 2002). The chemical composition of groundwater is controlled by different aspects which are mineral dissolution, evapotranspiration and anthropogenic activities or mixture of these processes. (Fass et al., 2007, Mapoma et al., 2014). Chemical elements that are found in ground water are influenced by factors such as pH variations, redox conditions, optimal temperature, and respiration. Study conducted by Smedley and Kinniburgh show that Ph, redox potential, and physical factors influences the potential toxic elements to mobilize (Smedley and Kinniburgh, 2002). Different elements require different conditions to degrade and for preservation, other require oxidizing conditions whereas other require the reducing conditions. The characteristics of an element, concentration, bio accumulation and duration of exposure can influence the strength of an element to cause harm in human being health, elements that are readily soluble have a high possibility to cause danger to human health (Smedley and Kinniburgh, 2002).

1.4 Aim of the research

The main aim of this research study is to assess minor ions and trace elements chemistry in groundwater in Luvuvhu catchment. As the study region is predominantly covered by the agricultural lands, this study can provide the baseline data for groundwater contaminants resulted from irrigation activities.

1.5 Objectives

- To determine the spatial and temporal variation in the minor ion and trace metal chemistry of groundwater
- To understand the causes for presence of minor ions and trace elements in groundwater
- To determine the possible geological and anthropogenic sources of trace elements.
- To assess the suitability of groundwater for drinking using national and

international standards

1.6 Problem statement

In South Africa 74% depend on groundwater for domestic use and with such a huge percentage of people depending on groundwater, it poses a problem of declining groundwater resources. Long term population growth and economic development are placing increasing pressure on South Africa's freshwater supply. The current climate changes often involve uncertain consequences for aquifer systems and the associated groundwater, it is expected that the stress on water will increase even further.

Groundwater quality and quantity problems in South Africa are mostly related to human activities such as industry and mining, urbanisation and deteriorating standards in wastewater treatment, agricultural drainage, land use patterns and waste disposal, all of which affect both human well-being and ecosystem functioning. For example, high rates of nitrate contamination can be found around urban centres and in the high-density rural settlements of the Northern Cape, Northwest, and Limpopo provinces (Tredoux et al., 2009).Groundwater is the main source of water for domestic and irrigation uses in the villages around the study area. The study area traditionally depends on agriculture with activities such as vegetables irrigation and forestry continuing year-round. The most common type of pollution in the catchment is non-point which originates from the surrounding farms. Also contributing towards groundwater pollution in the area are the surrounding rural settlement areas. Villagers in the areas also practice subsistence farming both irrigation and animal farming (cows and goats). Another major contributor to groundwater contamination is bad sanitation practices from the surrounding settlements (DWA ISP, 2012). The Limpopo province is one among the rural provinces that are facing water supply issues. The limited water resources have aggravated contamination further leading to freshwater crisis, especially for domestic purposes. Most people in the study area depend on groundwater to supplement the hugely over abstracted dam. Luvuvhu catchment is a semi-arid region, which is situated at the lower Limpopo basin. Evaporation rate is reported to be higher in the arid regions, which is noted in the water chemistry of the region. Evaporation causes salts like calcite, halite, and gypsum to precipitate in the soil and unsaturated zone. Precipitated salts can leach into groundwater by irrigation or rainfall (Tedaldi and Loehr 1992). Agriculture is the predominant activity in the area, which causes a huge demand on Albasini water scheme that acquires water from Albasini dam. Groundwater pollution is mainly due to excessive nutrients from agricultural lands. Effects of irrigation and fertilization can increase the amount of nutrients in the soil which further infiltrate into groundwater increasing its concentration in groundwater (Stigter et al. 1998). Major nutrients that result from agricultural lands are nitrate, phosphate, and potassium, ammonium, and fluoride (Nolan 2001; Oren et al. 2004).

1.7 Thesis outline

This report has seven chapters and details given below:

Chapter 1: Introduction

This section introduces topic and explains the present problems in the study region. It incorporates the quality of groundwater in the study region, aim of the research, objectives, problem statement and the importance of the study and research outline.

Chapter 2: Literature Review

This section looks at the literature review associated to the study of assessment of minor ions and trace element chemistry and previous studies conducted in the study area.

Chapter 3: Description of the study area

This chapter designates the study area details focusing on climate, topography, rainfall, drainage, geology, hydrogeology, land use activities.

Chapter 4: Methodology

This chapter emphasizes on the methodologies used for taking water samples, the instruments that were used in analysing and interpreting data. This looks at the instrumentation used in the laboratory and in the field (ICP spectrophotometer, Ph meter)

Chapter 5: Occurrence and distribution of nutrients and trace metals in the groundwater in an intensively irrigated region, Luvuvhu catchment, South Africa

Chapter 7: Conclusion

This chapter discusses the outcomes of the study and also looks at the recommendations that can be drawn from the study outcomes.

Chapter 8: References

References of literatures which were reviewed.

2. Chapter Two

2. Literature review

This section will review literature on groundwater quality and factors affecting groundwater quality based on minor ions and trace element chemistry in groundwater.

2.1 Groundwater quality

Chapman (1992) concluded that naturally the composition of groundwater depends on geological characteristics of the aquifer, speed of circulation across the aquifer, initial composition of infiltration water and movement rules of the transported substances in aqueous media, as well as the hydrodynamic factors. Groundwater resources are generally less susceptible to pollution than surface water and are considered the best supply for drinking water, however in many parts of the world people suffer from poor drinking water quality. Tiwari et al (2013) said the quality of groundwater depends on the composition of recharging water and the mineralogy of the geological formations in the aquifers. They further emphasized that it is important that people test water from the boreholes before using it for drinking and agricultural purposes even though the groundwater is considered clean, pure, and harmless (Tiwari et al., 2013). Harter (2003) reported that groundwater may contain natural substances in high concentration that can render it unfit and harmful for drinking and use for agricultural purposes (Harter, 2003).

When groundwater is moving its chemistry is affected by dissolved substances along the ground. This also depends on other factors such as temperature, pressure conditions underground, types of rocks and soil formations through which it is passing as well as residence time (DWA, 2010). The impact of human activities and the environmental parameters may also affect the geochemical mobility of certain constituents in groundwater (Chenini and Khmiri, 2009).Most of our daily activities contaminate surface water, air and land for example sewage disposal, pollution from power generation, mining and dissemination of chemicals and microbial matter at the land surface and into soils, or through injection of wastes directly into groundwater (Harter, 2003).

The most predominant forms of groundwater pollution from nonpoint sources are salt and nitrate contamination which adversely affect water wells followed by pesticide and industrial contamination. Surface water pollution can degrade groundwater and reduce quality of groundwater and pollution of groundwater can also degrade surface water. (USGS, 2015).Study conducted by Vetrimurugan et al established that in most cases shallow wells turn to have a high concentration of ions than deep wells, this is due to human activities such as agriculture. Increased concentration of nitrate due to agrochemicals use can affect the suitability of groundwater in domestic use (Vetrimurugan et al, 2017).

2.2 Hydrogeochemistry of groundwater

Groundwater experiences many chemical processes while travelling along its path. The chemical composition of groundwater indicates these processes. Precipitation, evapotranspiration, chemical composition of recharge water, interaction with gases within unsaturated zone, mixing of different groundwater and surface water are some of the processes that influence groundwater chemistry (state of Oregon DEQ, 2004).Precipitation increases components concentration of groundwater (Winter et al, 1998). According to Hem (1985) precipitation is mixed with small concentrations of atmospheric components such as dissolved gases and salts. Some of the constituents involved are Nitrate, sulphate, calcium, and sodium. Chemistry of surface water bodies is influenced by many activities both natural and human activities. Surface water bodies' chemistry is influenced by agricultural return flows, runoff, rainfall, wastewater and other activities. Seepage water is affected by some of the activities that impacts on groundwater chemistry (State of Oregon DEQ, 2004).

Evapotranspiration is high in arid regions; its impact on chemistry in these regions is highly noticeable. Studies conducted by Tedaldi and Loehr (1992) depicted that evaporation causes salts like calcite, halite, and gypsum to precipitate in the soil and unsaturated zone and precipitated salts can be reached by irrigation or rainfall . The surrounding rocks react with water and give its characteristic chemistry. Rocks containing silicate minerals do not react with most groundwater readily. Even so carbonate minerals on these rocks react with water and play a vital role in groundwater chemistry (Tiwari et al., 2013). Srinivasamoorthy et al. (2012) studied the hydrochemistry of groundwater in Tamilnadu India and portrayed that the chemical composition of groundwater is controlled by many factors including the composition of the precipitation, geological structure, mineralogy of the watersheds, aquifers, and geological processes within the aquifer along with influence of external pollution agencies like effluents from agricultural return flow, industrial and domestic activities.

Geology and geochemical processes are natural factors that affect the quality of groundwater. Minor ions in groundwater are controlled by hydrogeochemical processes such as, weathering, dissolution, mixing, ion exchange (Rajmohan and Elango, 2004). Trace elements are affected by geochemical factors such as oxidationreduction conditions the presence of ions that form soluble complexes with metals, evaporative concentration, and mixing and dilution (Drever, 1988; Hem, 1992).

Zhang et al (2014) studied groundwater chemistry of semi-arid region and found out that effluents from municipal wastewater, mining and industrial activities causes pollution even if they are treated, these waste water influences groundwater hydrochemistry. Activities such as industrialization, urbanization, agricultural irrigation, water pollution, and changes in irrigation practices (e.g., the channel line project and dredging of discharge ditches) influence the phreatic water resources and alter water hydrochemistry. Most common types of water pollutants are pathogenic organisms, synthetic organic chemicals, inorganic chemicals, oxygen-demanding wastes, plant nutrients, sediments, radioactive substances, oil, and heat (Zhang et al., 2014). Population expansion and excessive exploitation of groundwater influences water chemistry and hydro chemical characteristics of natural water in the study region. According to a study conducted by USGS (2015) human activities interference has created complicated spatial-temporal changes in the quantity and quality of groundwater while creating a whole new artificial ecosystem (USGS, 2015). Trace elements are defined as constitutes that are less than 0.1 mg/l (Domenico& Schwartz, 1990).Naturally soils contain considerable amounts of naturally occurring soluble trace elements. They are influenced by the soil parent material, climate, and vegetation. The trace element composition of groundwater depends not only on natural factors such as the lithology of the aquifer, the quality of recharge waters and the types of interaction between water and aquifer, but also on human activities, which can alter these fragile groundwater systems, either by polluting them (Helena et al., 2000). Studies conducted in 2006 to 2007 in the study area by Brink (2009) and analysis indicated that in Luvuvhu catchment trace elements Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb detection limits were 0.1 µg/l for all of them. Metals such as arsenic, barium, cadmium, chromium, lead, mercury, tin, selenium, and silver may be found in a variety of water treatment chemicals. These facilities strongly affect the quality of the stream for long distances downstream. Point sources of contamination that affects ground water can include septic tanks, fluid storage tanks, landfills, and industrial lagoons (Winter et al., 1998).

John and Trollip (2009) investigated the national standards for drinking water treatment chemicals and reported that most chemicals found in drinking water cause chronic health problems rather than acute health problems. These health effects begin to noticeable after continued drinking water. Hanson (2000) announced that chemical pollution of groundwater sources could have detrimental effects on human and animal health. Some trace elements are of concern these include arsenic, boron, lead, cadmium, chromium, copper, molybdenum, nickel, selenium, and strontium (Hanson, 2000).

Trace elements such as cadmium, lead, nickel are harmful to human beings in high concentration (Khan, 2011). Long term exposure to nickel causes respiratory problems, heart and liver damage and skin irritation. The annual reports of National Research Council (1999, 2001) affirmed the limit of arsenic in drinking water at 50 μg/l, however, the US federal drinking water standard, or maximum contaminant level (MCL), was brought down to 10 μg/l. According to the World Health Organization (WHO), the provisional limit of arsenic in drinking water is 10 μg/l, and the same limit was adopted by the European commission (WHO, 2006).The presence of copper in trace concentrations is essential for the formation of haemoglobin. Overdose of copper leads to neurological diseases such as hypertension, liver, and kidney dysfunctions (Krishna and Govil, 2004). Ingestion of copper causes infant death, short lived vomiting diarrhoea etc. (Barzilay, 1999).

Trace elements are considered to be the most important environmental factors in plant ecology (Zhang et al., 2006). Plant tissue studies done by Zhanbin et al (2013) in Shaanxi, China have shown that trace elements are an important factor in crop growth and if they are found to be excessive or less plant growth is affected. The presence of trace elements in groundwater is of general concern looking at their importance in both animal nutrition and plant growth. Trace elements are the most studied elements in plants and foodstuffs. Trace elements such as titanium, vanadium, cobalt, nickel, aluminium, silicon, arsenic, selenium, fluorine, and iodine have been evaluated covering absorption, transport and accumulation, biochemical functions, deficiency and toxicity and their effects on plant growth (Aller et al., 2006).

Domenico and Schwatz (1990) defined Minor ions as constituents that are 0.01 mg/l to 10 mg/l. Naturally, groundwater contains minor ions. As the water travels along the rock mineral formations, it slowly dissolves these ions from soil particles, sediments, and rocks in the pores or fractures of the unsaturated zone and the aquifer. Some dissolved solids may have originated in the rainwater or river water that recharges the aquifer (Satapathy, 2009). In water all the dissolved solids are either positively charged ions (cations) or negatively charged ions (anions). The total negative charge of the anions always equals the total positive charge of the cations (Harter, 2003). Tiwari et al (2013) study of major and trace elements in groundwater of Birsinghpur are, Satna district Madhya Pradesh in India indicated that minor ions can be regarded as essential to human beings and for irrigation. However, concentration plays a major role in ground water chemistry. Minor ions such as Iron are regarded as essential in human beings' health, however high concentration of iron causes a bad taste, staining and operational problems in water supply (Tiwari et al, 2013). Minor ions are Br, Li, F, NH4, NO3 and PO4 (Harter, 2003). Brink (2009) investigated the effects of DDT on aquatic organisms in Luvuvhu river and found out that minor ions in Luvuvhu catchment along Luvuvhu river particularly Albasin dam show that in 2007 to 2008 the following minor ions Ammonia, Nitrate, phosphate were higher, Ammonia was found to be slightly elevated and suspected to be from agricultural practices in the surrounding area.

In Luvuvhu catchment the main concerns are high levels of nutrients and ammonia downstream of urban areas, and bacteriological contamination. Quality of water of the Luvuvhu River is largely affected by intensive agriculture of sub-tropical fruits and afforestation in the upper catchment, the urban sprawl of Thohoyandou in the middle catchment. High phosphate values occur in a large part of the catchment and into the Kruger National Park. Phosphate values are higher due to the use of fertilizers for the intensive agriculture in the catchment and also domestic wastewater treatment plant effluent from Thohoyandou and the surrounding unserviced rural settlements. In the middle to lower Luvuvhu water quality show a deterioration of phosphates, nitrates, and ammonia (DWA ISP, 2012).

2.3 Impact of agriculture on groundwater quality

Studies conducted by DWA ISP (2012) concluded that agriculture is one of the largest human activities in Luvuvhu catchment. It has been the biggest cause of landscapes modification throughout the world. Ploughing of land affects infiltration and runoff characteristics of the land surface and affects ground water recharge, delivery of sediments to surface-water bodies. These processes whether directly or indirectly they affect surface water and groundwater interaction. Agricultural activities that are affect ground water and surface water are irrigation and application of chemicals to cropland (Winter et al., 1998). Agriculture requires good quality water rich in mineral constituents for good quality production, hence groundwater should contain such mineral to be suitable for agricultural use (Vetrimurugan & Elango, 2015). Nutrients are important in irrigation because they increase plant health and growth, however too much of it can alter the quality of water (USGS, 2010)

Winter et al (1998) reported that in order to prevent too much build-up of salts in the soil, irrigation water is used to dissolve and flush out build up salts into groundwater. Return flows from irrigation reach high concentration of dissolved solids and degrade the quality of groundwater. Uses of pesticides and fertilizers in irrigation result in pollution of water resources. Some pesticides used in irrigation are slightly soluble in water and attach (sorb) to soil particles. Other pesticides are detected in low but significant concentration in both groundwater and surface water is found. Ammonium is a major component of fertilizer and manure used in agriculture and is very soluble in water. Increased concentrations of nitrate that result from nitrification of ammonium can cause an increase in nitrate concentration in both groundwater and surface water in agricultural lands. Livestock farming also contribute to contamination of both ground and surface water (Winter et al., 1998).

The Luvuvhu catchment is dominated by agriculture predominantly banana, citrus fruit, macadamia nuts and avocadoes. The catchment also have a few industries mostly processing and warehouses. There are three warehouses for processing and packing macadamia nuts which process about 6500 tonnes of nuts in a year. There are two more processing warehouse in the catchment which process citrus fruit (Visser, 2003).

2.4 Geological influence on groundwater chemistry

The knowledge of the nature of the bedrock geology is important in trying to determine groundwater quality in a certain area. In other countries the bedrock contains sedimentary layers that are rich in pore spaces between mineral grains. Some areas of the world, bedrock consists of sedimentary layers that have abundant pore spaces between individual mineral grains (Evans, 2010).

Groundwater moves very slow while moving underground which allows for a considerable amount of time for water to be in contact with surrounding rock formation. In most of the aquifers the geological components are made up of minerals that are able to dissolve slowly while in contact with water. Overtime because groundwater moves slowly in the aquifer it will accumulate dissolved materials from the rock (Earl, 2015).

The geology of some of the areas contains a variety of minerals that are able to cause problems in the quality of water (Evans, 2010). Some of the minerals that are found in the rock or sediment have a potential of contaminating the water with various elements to a point wherein water can be less fit for human consumption and for agricultural use. In most cases if the aquifer has high levels of particular element, it can affect the quality of ground water that passes through it by increasing the concentration of the element in question (Earl, 2015).

Examples could be the arkosic sandstone which is typically found in The Triassic Newark Group of Connecticut in America. This particular sandstone usually contains a mixture of potash feldspar, quartz, and granitic rock fragments. This rocks usually contain 60–70% silica (or silicon dioxide), 10–15% aluminium oxide (Al_2O_3), potassium (K), sodium (Na), and various other elements (Bissell et al, 2018)

Other areas are comprised of Lithic arenites which are mostly rich in mica. This rock can contain 60-70% of silicon dioxide ; 15 % of aluminium oxide; and potassium (K), sodium (Na), iron (Fe), calcium (Ca), and magnesium (Mg) (Bissell et al, 2018).

3. Chapter three

3.1 Study area

The study area falls in the Lowveld of the province which forms part of the greater Limpopo River basin (Figure 1). According to the Koppen Classification the basin is predominantly semi-arid (M'marete, 2003). The study area lies between 30º 09"58E and 23º05" 485'E. The study area catchment is 581 km^2.The major river within the area is Luvuvhu River which flows in easterly direction to the Kruger national park and to Mozambique Channel. Figure 1: map showing the study area. The study area is situated in South Africa, Limpopo province under Luvuvhu catchment. It stretches from rural towns such as Elim, Sibasa, and Thohoyandou as the main town. Agriculture is the most dominant activity in the catchment.

3.2 Geology and soil type of the area

The geology of the study area falls within the Soutpansberg group which is of the Mokolian age. Geological features in Luvuvhu catchment have contrasting rock types; these include quartzite, sandstone, mudstone, shale, and basic lavas (South Africa RHP, 2015). The Soutpansberg rocks contains dykes and diabase in high quantities (Brandl 2003). The Soutpansberg mountain is comprised of sedimentary rocks and basaltic lavas (Limpopo State of the Environment report: Phase 1, 2004). The Levubu area consists of alternating sandstones and shale with feldspathic greywacke and conglomerate and arkoses at base (Jansen 1975).

Soil of the study area is predominantly deep (>1 500 mm), dystrophic, red, and yellow well-drained clays with apedal structure. Clay content is generally high (60%) and soil reaction is acidic (pH 5). They are classified as Hutton form (South African System of Soil classification) (Soil Classification Working Group, 1991), Rhodic Eutrustox (Soil Survey Staff, 2006) or Rhodic Ferralsol (WRB, 2006).

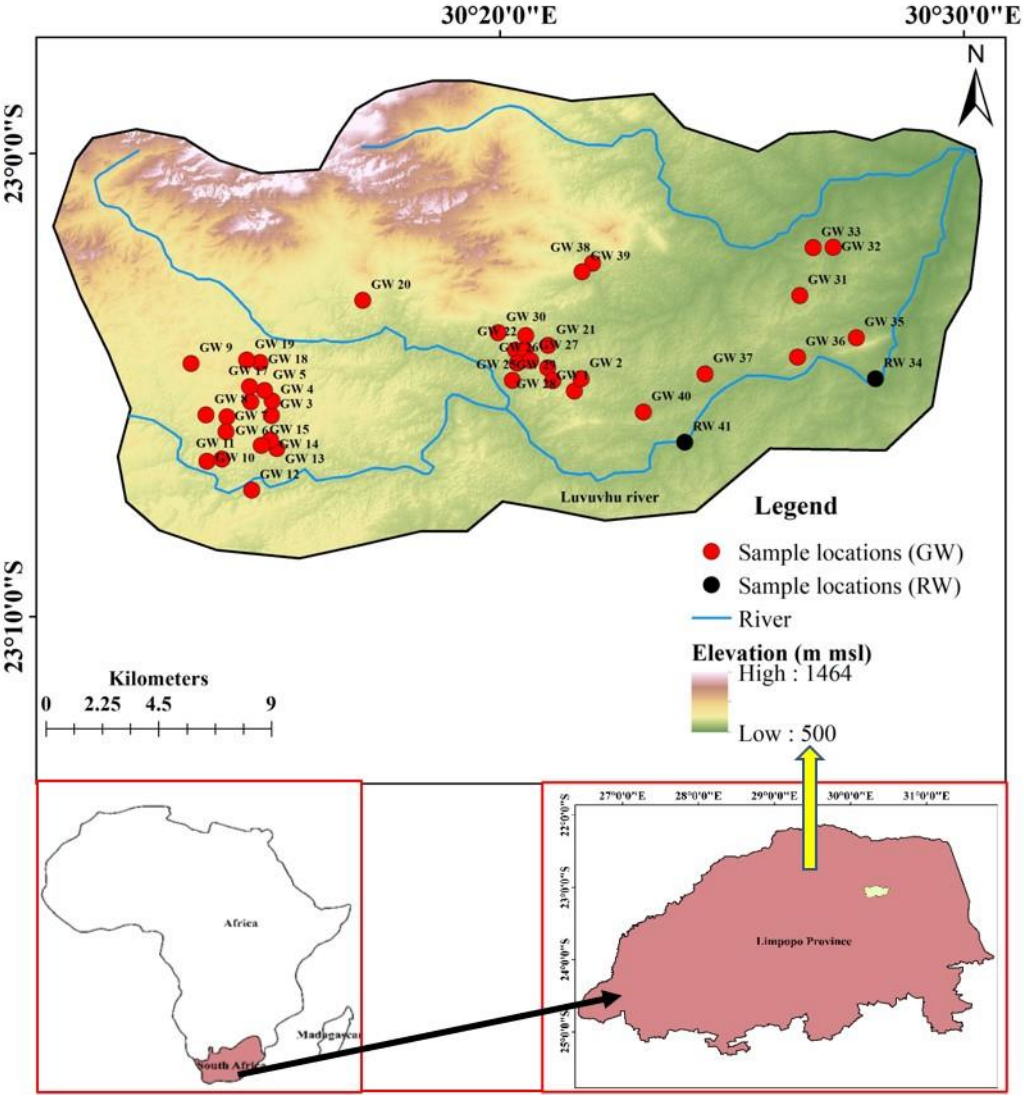

Fig 1: Map of the study area

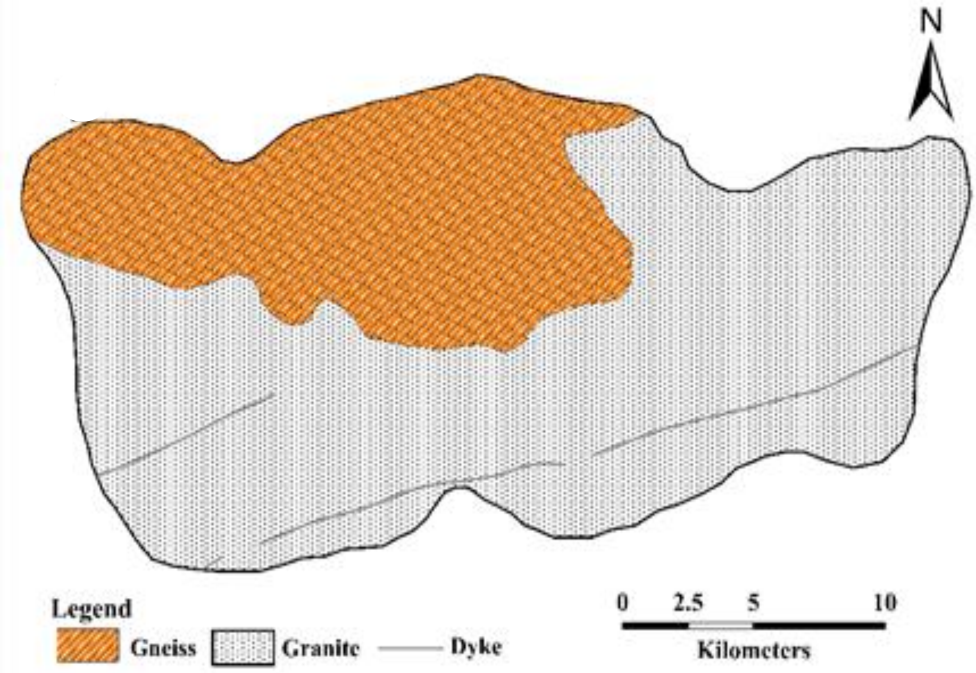

Figure 2: Geology map

3.3 Geohydrology and drainage of the study area

The catchment is named after the main river which is Luvuvhu river of which the whole catchment drains into (Odiyo et al, 2012). The Luvuvhu river flows into Albasin and Nandoni dam and drains in the Kruger national park. Luvuvhu river falls into Limpopo river and drains into the Mozambique channel. The river is comprised of a few tributaries which include Lutonyanda, Dzindi, Mvudi, Mutshundudi and Mbwedi etc. Along the river agricultural activities are dominant together with brick making and sand mining especially in Nandoni dam and upstream of the dam. With the disturbances caused by sand mining and brick making agriculture depends on groundwater in winter season.

3.4 Climate and rainfall

The climate in South Africa ranges from desert and semi-desert in the northwest of the country to sub-tropical on the eastern coastline. Luvuvhu catchment has the highest average monthly amount of rainfall received; it is received normally from November to March every year (Mpandeli, 2006). February usually records the highest rainfall of more than 184 mm; winter months starts from May to August however May and August months have slightly high temperatures. Winter season climate is warm during the day with dry air prevailing in Vhembe. Temperature can drop sharply in the evenings. During the winter period, less than 20 mm of rainfall monthly is usually received in the catchment with the average rainfall dropping to 8 mm during August in 2003 (Mpandeli, 2006). Daily temperatures at Thohoyandou vary from about 25˚C to 40ºC in summer and between 22˚C and 26ºC in winter. When the temperature is high, there is also a high probability of evaporation during that particular period. Average temperatures recorded are shown in table 1.

Table 1: Average temperatures in Luvuvhu catchment

Average temperature's (°C) in Limpopo				
City	Summer (January) Maximum	Summer (January) Minimum	Winter (July) Maximum	Winter (July) Minimum
Thohoyandou	31	20	24	10
Luvuvhu	18	28	12	25

3.5 Land use

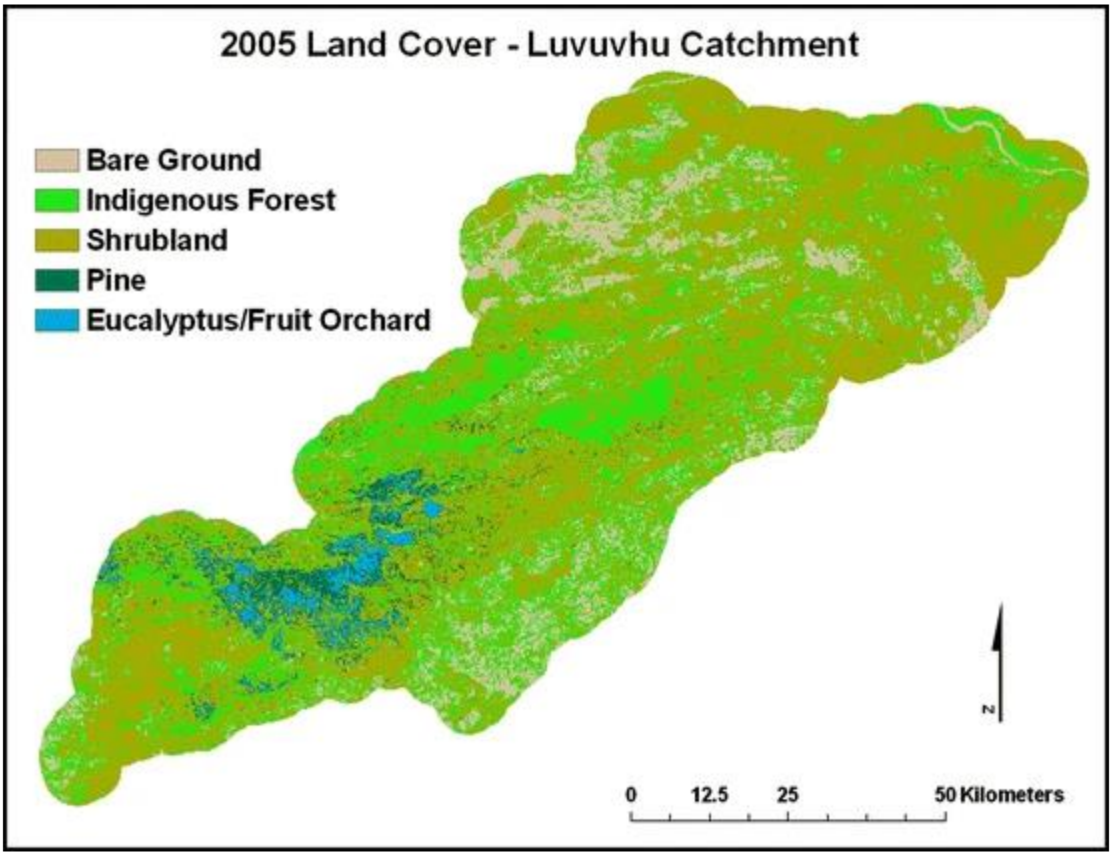

Figure 3: Land use map of the study area (source: Griscom et al., 2010)

Major land use activities include commercial agriculture which is 20% and is dominated by banana, mangoes, avocadoes, and macadamia farming. Forestry which is estimated at 11% and the plantation covers 44% of the upper reaches of the Luvuvhu and Latonyanda rivers and decreases to less than 10% towards the Albasin Dam. Subsistence farming is about a third of the total agricultural component (South Africa RHP, 2015). Agriculture is the major source of income for most people in the catchment.

3.6 Topography

The Luvuvhu River starts from Soutpansberg Mountain in the southeast side of the catchment approximately 20 km south of Louis Trichardt town. Drakensberg Mountain extends towards the western part of Limpopo. The Luvuvhu catchment is generally sub-tropical, although mostly semi-arid to arid. (DWA, 2006).The slopes in the area are 15^0 with relief of more than 1m (DWA, 2006). Altitude within the catchment ranges from 450 meters to 1 425 meters above sea level. The catchment receives high rainfall due to its topography, which influences hydrology of the area.

4. Chapter four

4.1 Research methodology

In order to achieve the set objective groundwater chemistry of the area groundwater samples were collected according to the accessibility of wells in the catchment.

4.2 Data collection

At time of collection sample pH will be adjusted to pH <2 with nitric acid (HNO_3).The bottles were labelled properly to avoid confusion after sampling the bottles were transported to the University of Zululand and stored in a cool dark place until analysis. Samples were taken in two seasons firstly being the rainy summer season and in dry winter season. Finally, all measured chemical parameters were compared with the world health organisation and South African drinking water standard. Groundwater samples were collected from 39 boreholes and 2 surface water samples from Limpopo River during the month of August 2017 (Figure 1). Prior to sample collection, the boreholes were pumped for five minutes to remove stagnant water (purging). Water sampling was carried out after the stabilisation of field parameters namely temperature, dissolved oxygen (DO), pH and electrical conductivity (EC). Field parameters were measured on the field using potable digital meters (Aqua probe A-700). Depth to groundwater level was measured using a water level indicator. Water samples were collected in duplicate using precleaned HDPE bottles and rinsed again with source water before sampling. Samples were stored at 4°C and transported to the University of Zululand hydro geochemistry laboratory for further analysis. Samples collected for trace metal analysis were filtered using 0.45µm membrane filter to remove suspended material and acidified with nitric acid (pH<2) before analysis to prevent precipitation of the trace metals.

Water quality data was obtained from the Department of water and sanitation. Rainfall data for a period of 20 years will be obtained from South African Weather Service. Field parameter such as Groundwater level were recorded using a water level meter (Solinst 100). EC and pH and temperature were measured in the field using portable digital measuring devices.

4.3 Data analysis

Samples were filtered and directly introduced into ICP-MS instrument by conventional pneumatic nebulization, using a peristaltic pump with a solution uptake rate of about 1 ml/min. The nebulizer gas flow, sample uptake rate, detector voltages and lens voltage was optimized for a sensitivity of about 50,000 counts/s for 1 ng/ml solution of In. The instrument was calibrated using five calibration solutions ranging 0-5 mg/L for Al, Cd, Cu, Fe, Zn, Pb, Cr, Mn, B, Li, Ag (Weaver et al, 2007), (Sundaram, 2009). Groundwater sample analyses were followed according to guidelines established by the American Public Health Association (APHA 2005). Five trace elements such as Cr, Zn, Pb, B, Si and Li were analysed in the laboratory using inductively coupled plasma-mass spectrometry (NexION 2000 ICP-MS). Nutrients such as potassium, nitrate, ammonia, phosphate, and fluoride were analysed using Ion chromatography (Metrohm 930 Compact Flex). Standards and blanks were run regularly to confirm the accuracy of the ionic concentration. The accuracy of the analysis was determined by calculating the Ion balance error, which was generally less than 5%.

4.3.1 Software used

The GIS software was used to create different kinds of maps by using geodatabases. MS Excel software will be used for data interpretation. Aquachem software will be used for geochemical plots and graphical techniques for Piper and Wilcox diagrams. ArcGIS v10.5 was employed to prepare the study area map, sample location map, drainage map, land use map spatial distribution maps of various ions using the inverse distance weighted (IDW) interpolation technique. It is termed as inverse distance weighted because as the distance from the unknown point increases, the weight decreases (Almodaresi et al. 2019; Vetrimurugan et al. 2017). IDW technique has been widely used by several researchers and has been proven successful in the characterization of spatial variability between sampled points and mapping of potential areas of risk to groundwater contamination. The IDW interpolation technique uses linear combination of weights at known points to estimate the unknown location values (Shobha 2018; Ogbozige et al. 2018). Shepard (1968) expresses IDW as.

$$z = \frac{\sum_{i=1}^{n} w_i z_i}{\sum_{i=1}^{n} w_i} \tag{1}$$

$$w_i = \frac{1}{d_i^{\,p}} \tag{2}$$

where z is the interpolated value, z_i is the known value, n is the number of known values used in interpolation, d_i is the distance between known and unknown values, and p is the power parameter where weight declines as the distance increases from the interpolated values.

5. Chapter five

Results and discussion

5.1 Introduction

Nutrients in the water are mostly derived from anthropogenic activities rather than soil and rock materials. In the agricultural region, groundwater is largely affected by fertilizers and pesticide application and irrigation return flow, which in turn enhances nutrients load and salinity in groundwater (Stigter et al. 1998; Vetrimurugan et al. 2017; Rajmohan 2020). Nitrates, phosphates, ammonia, and potassium are the most common nutrients that are associated with groundwater contamination derived from fertilizers used in irrigation activities. The content of nutrient in groundwater is usually related to the number of fertilizers used for crops in the croplands. To stimulate or increase crop yields, farmers tend to increase the use of agrochemicals (Lwimbo et al. 2019). However, excess application of fertilizers could negatively impact the groundwater quality. NPK (nitrate, phosphate, and potassium) are common nutrients in groundwater originated from fertilizer application (Stigter et al. 1998; Shamrukh et al. 2001; Agca et al. 2014; Lawniczak et al. 2016; Rajmohan et al. 2017).

Soil contains considerable amount of naturally occurring soluble trace elements (Edet et al. 2014; Basahi et al. 2018). They are influenced by the parent material, climate, and vegetation. The trace element composition of groundwater depends not only on natural factors such as the lithology of the aquifer, the quality of recharge waters and the interaction between water and aquifer, but also on human activities, which alter these fragile aquatic systems, either by polluting them (Helena et al. 2000). Excessive application of fertilizers in agricultural areas is one of the major sources of trace metals in groundwater (Lwimbo et al. 2019). The use of excess fertilizers results in a decrease in soil pH, which further promote availability of trace metals (Khan et al. 2018). Contamination of groundwater by trace metals can have serious impact on human health (Wagh et al. 2018; Mthembu et al. 2021).

In South Africa, the demand for freshwater exceeds the supply due to water scarcity problems faced in the country. Groundwater chemistry in the Luvuvhu catchment was largely controlled by mineral weathering, reverse ion exchange and irrigation return flow (Nethononda et al. 2019). Increasing the heavy metal concentration in the geothermal spring and soil has enrichment of vegetation in surrounding areas and rock-water interaction (Durowoju et al. 2016). The potential harmful trace elements in groundwater of Greater Giyani, Limpopo, inferred that arsenic poses greater influence in groundwater quality due to bedrock mineralisation (Munyangane et al. 2016). Natural and anthropogenic activities were responsible for heavy metal contamination in groundwater. This could raise the potential health risk for children and adults.

5.4 Results and discussion

Results of the physio-chemical analysis of the water samples taken in the study area are illustrated in Table 2. Groundwater pH in the study area ranges between 6.0 to 7.6 with a mean value of 6.6. In the study region, groundwater pH is less than 7.0 in most of the samples and acidic in nature. Figure 4 shows that groundwater in the upstream region is acidic whereas it is greater than 7 in the downstream region. According to WHO (2011), 51% of samples are not potable due to low pH (pH<6.5) in the study region. However, according to South African drinking water standards (DWAF 2015), all the samples are suitable for drinking.

IDW interpolation tool of ArcGIS was applied to achieve the spatial distribution maps of the study area. The results of the IDW interpolation showed that electrical conductivity (EC) ranges from 81 µS/cm to 1206 µS/cm with a mean value of 358 µS/cm. EC in this aquifer is less than 1000 µS/cm except one well, and it is less than 500 µS/cm in 82% of samples. The results of the IDW interpolation revealed total dissolved solids (TDS) varies from 53 mg/l to 784 mg/l with an average value of 233 mg/l. Likewise, EC and TDS in the river water are 159 µS/cm and 103 mg/l, respectively. Further, the groundwater TDS is less than 500 mg/l in 92 % of samples. The EC and TDS concentrations in the groundwater indicate that groundwater is less mineralised and fresh in nature. According to WHO (2011) and DWAF (2015), TDS in 3 and 6 samples exceeded 500 mg/l and 450 mg/l, respectively recommended for drinking in the study region (Table 2). The spatial distribution of EC and TDS illustrate that it is also behaved like pH and higher values are noticed in the downstream wells (Figure 3). Dissolved oxygen (DO) in groundwater varied from 2.0 mg/l to 3.2 mg/l with an average value of 2.3 mg/l. Standard limit for DO in drinking water has not been established.

5.4.1 Nutrients chemistry

Nutrient concentrations in groundwater are mostly associated to land use particularly fertilizer applications, human and animal wastes, etc. (Hantzsche and Finnemore, 1992). During infiltration to the vadose zone, recharge water picks up nitrogen and phosphorus retained in the soil and transport them further down to the water table. Aquifer with highly permeable soils is susceptible to contamination.

5.4.1.1 Potassium

Potassium in the study area ranges from 6 mg/l to 18 mg/l with an average of 11.4 mg/l. The potassium concentration in the groundwater shows that 31% of samples are not recommended for drinking which exceeded the WHO (2011) safe limit (Table 2). In contrast, all the samples are suitable for drinking based on DWAF (2015). Figure 3 shows that there is no specific trend in potassium concentration and distribution but groundwater in few pockets has high concentration.

Potassium is mostly originated from weathering of silicates and chloride minerals namely feldspars (orthoclase and microcline), carnalite and sylvite. Further, potassium compounds are also present in popular synthetic fertilizers (potassium nitrate, KCl, NPK), which are applied regularly during cultivation in the study region. Potassium is an essential dietary requirement for nearly all the organisms and plays an important role in plant growth (WHO 2009). Potassium is mostly retained in the clay soils through adsorption in the vadose zone, thereby depleting the potassium content in groundwater.

5.4.1.2 Nitrate

Concentration of nitrate in the groundwater is between 0.9 mg/l and 29 mg/l with a mean value of 6.7 mg/l. Ingestion of drinking water with high nitrate concentrations can cause many health concerns in infants such as methemoglobinemia (Mahvi et al. 2005; Khan et al. 2018; Lwimbo et al. 2019).

Adults on the other hand are at a high risk of developing gastrointestinal and bladder cancer due to exposure of elevated nitrate (Chotpantarat et al. 2020). Nitrate can cause low oxygen levels in the blood, a potentially fatal condition (Spalding and Exner 1993). In the study area, groundwater nitrate concentration is within the recommended limit for drinking prescribed by the WHO (2011) and DWAF (2015). Figure 3 depicts that low concentration is recorded in the upstream and middle stream regions. High concentration of nitrate is observed in the downstream region. In agricultural lands, nitrate is the primary form of nitrogen, which is soluble in water and can easily pass-through soil to the groundwater.

5.4.1.3 Ammonium

Concentration of ammonium in groundwater ranges from BDL to 3.9 mg/l and the recorded average is 0.9 mg/l. The ammonium concentration is less than 1 mg/l in 72% of samples.

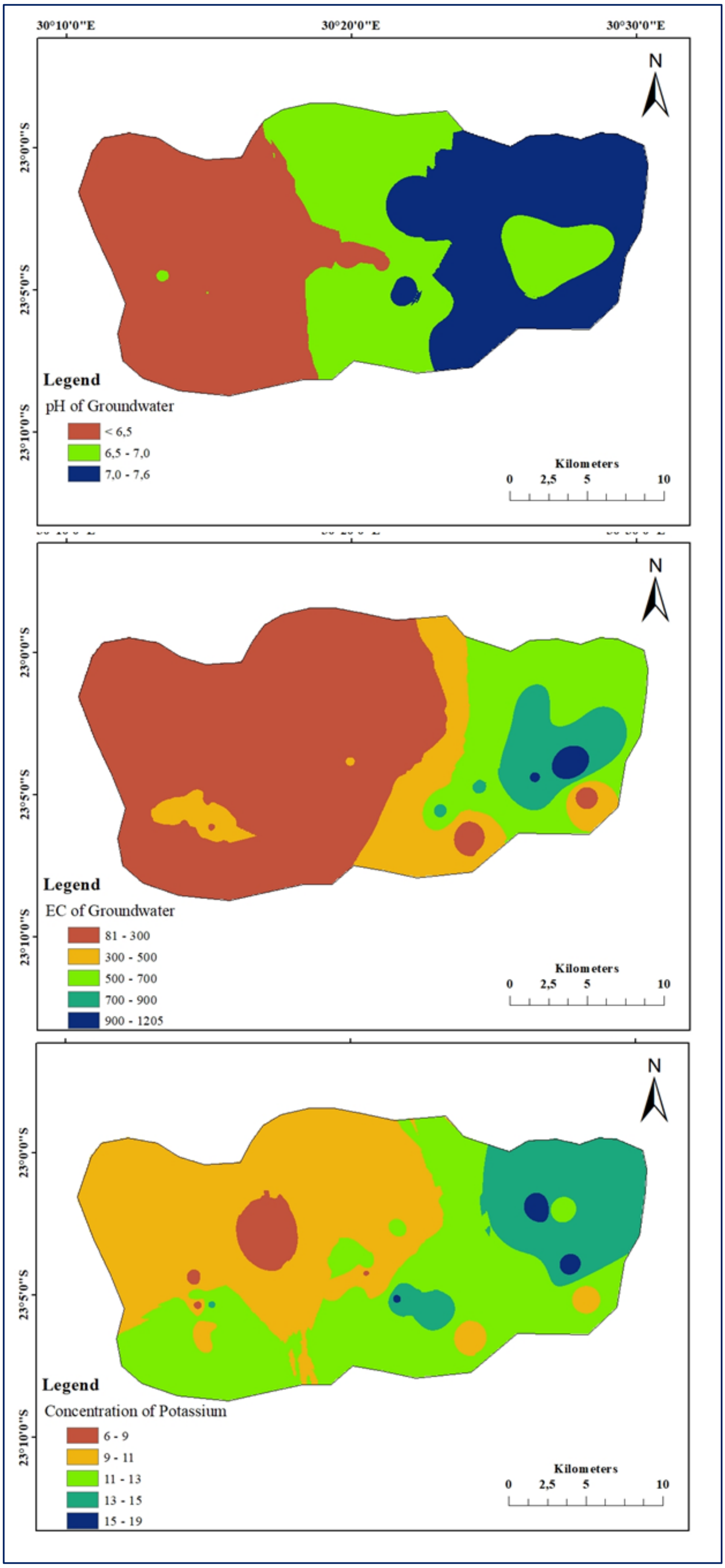

Figure 4. Spatial distribution of pH, EC (µS/cm) and K (mg/l) in the study area

Table 2 Statistical summary of the parameters analyzed in the groundwater and river water (RW) and their comparison with WHO and DWAF standards

	Min	Max	Mean	STD	River water (RW)	WHO (2011)	DWAF (2015)	No. of samples exceeded (%)	No. of samples exceeded (%)
pH	6.0	7.6	6.6	0.4	7	6.5-8.5	6.0 - 9.0	20(51)	
EC	81	1206	358	243	159	-	-	-	6 (15)
					Unit (mg/l)				
TDS	53	784	233	158	103	500	450	3(8)	6 (15)
DO	2.0	3.2	2.3	0.2	3.0	-	-	-	-
K	6	18	11.4	2.6	10	12.0	50	12(31)	0
SO_4	2	19	6.5	4.1	2	250	200	0	0
NO_3	0.9	29	6.7	6.6	1.80	45	45	0	0
NH_4	BDL	3.9	0.9	1.1	0.17	-	-	-	-
PO_4	0.2	7.3	1.0	1.1	0.50	-	-	-	-
F	BDL	1.5	0.5	0.3	0.08	1.5	1.0	1	2(5)
Si	1.0	9.0	5.8	1.8	0.10	-	-	-	-
					Unit (µg/l)				
Li	185	322	218	22.4	203	-	-	-	-
Pb	68	418	196	69.6	209	10	10	39(100)	39(100)
Zn	0	813	106	224	0	5000	3000	0	0
B	0	92	12	21.1	0	2400	-	0	0
Cr	23	44	34	3.7	33	50	50	0	0

The spatial distribution also shows that ammonium concentration in most of the study region <1 mg/l and higher values are recorded in the downstream region (Figure 4). In irrigation lands, urea, ammonium fertilizers and organic manures are used as a source of nitrogen for crops, which are likely to increase ammonium concentration in the groundwater through irrigation return flow. In fact, ammonium is mostly retained in the clay or humus soil, which reduce leaching. Natural levels of ammonium in the groundwater is usually below 0.2 mg/l (WHO 2009). In general, in areas of active landfills, septic tanks and or in sewage disposal plants ammonium is released into subsurface and are produced as a result of anaerobic degradation of organic matters (Bohlke et al. 2006). Similarly, the excessive ammonium in the study region is caused as a result of septic tanks, sewage disposal and application of agrochemicals.

5.4.1.4 Phosphate

Phosphate concentration in the groundwater varies from 0.2 mg/l to 2.3 mg/l except one well with 7.3 mg/l. The average phosphate concentration is 1 mg/l and it is < 1 mg/l in 67% of samples. The spatial distribution pattern also indicates that wells in the upstream and downstream regions have low values whereas high phosphate is recorded in the central portion of the study region (Figure 4).

Groundwater with extremely high concentration of phosphate is not recommended for drinking due to various health problems namely digestive problems (Fadiran et al. 2008; Singh 2013). In water, phosphorus mostly occurs in the form of orthophosphate ion (PO_4^{3-}). Application of chemical fertilizers, manure and composed materials accumulated phosphate in soil. Phosphate is strongly adsorbed by soil colloids which impedes its leaching rate compared to NO_3^-. During wastewater infiltration and irrigation return flow, the adsorbed phosphorus in the soil will be dissolved and leached into the groundwater. However, movement of phosphorus within and below the root zone can be limited by adsorption and mineralization. Adsorption of phosphate is also limited by total surface area of clay in the soil. Studies also suggest that the site factors like soil texture and or phosphate saturation degree might control the adsorption of phosphate in spite of large application of fertilizers (Mabilde et al. 2017). Similarly, within the study area, the groundwater in upstream and downstream has low phosphate concentration due to adsorption processes in the vadose zone in spite of usage of fertilizers. Elevated phosphate concentrations in the central part of the study area where it may be owed to the application of phosphate containing fertilisers.

5.4.1.5 *Fluoride*

Fluoride concentration in the groundwater varies from BDL to 1.5 mg/l with an average value of 0.5 mg/l (Table 2). In the study area, fluoride in groundwater is less than 1 mg/l except in two wells. Fluoride in the river water is also very low (Table 2). Groundwater is suitable for drinking in the study region except two wells based on WHO (2011) and DWAF (2015) recommended drinking water limit (Table 2). The spatial variation of fluoride shows that there is no particular trend; however, lower values are noted in the centre of the study area (Figure 5).

Natural fluoride sources in the earth's crust are fluorapatite, fluorite, hydroxyapatite, cryolite and hornblende. Volcanic, gneissic, and granitic rocks are common geogenic sources of fluoride (Dehbandi et al. 2018). Phosphate containing fertilizers are also known to increase fluoride concentrations in soils and groundwater. Fluoride is used for dental preparations to assist in dental health problems especially in people with high sugar intake. Fluoride is also present in many types of food stuff such as brick tea which increases fluoride concentration in people consuming such food and water containing fluoride. High fluoride in groundwater is not recommended for drinking because it causes endemic fluorosis (Morales-Arredondo et al. 2016; Kebede et al. 2016; Vetrimurugan et al. 2013; Li et al. 2014). Further, calcification of ligaments and skeletal fluorosis are commonly reported in consumers with high fluoride in drinking water (Tiwari et al. 2013).

5.4.2 Trace elements

Trace elements are the most commonly known type of contaminants in groundwater. Trace element contents are derived from both natural and anthropogenic sources. Groundwater trace element concentration is controlled by different factors such as anthropogenic activities, soil characteristics, mineral composition of the rocks, aquifer properties, biogeochemistry of the aquifer system (Focazio et al. 2002; Frind et al. 2006; Jinwal et al. 2010; Tiwari et al. 2013; Mthembu et al. 2020). Many trace elements such as Fe, Mn, Cu, Zn, Co, and Ni are the micronutrients essential for the living things. The deficient of such micronutrient or excess causes different disorders in human body (Jinwal et al. 2010). In contrast, other trace metals such as Cd, Pb and Cr are toxic to human beings even if ingested in low concentration because of their characteristics to accumulate in the body (Domenico and Schwartz, 1998). In this study, occurrence, and distribution of trace metals such as Li, Pb, Zn, B and Cr were discussed in further section.

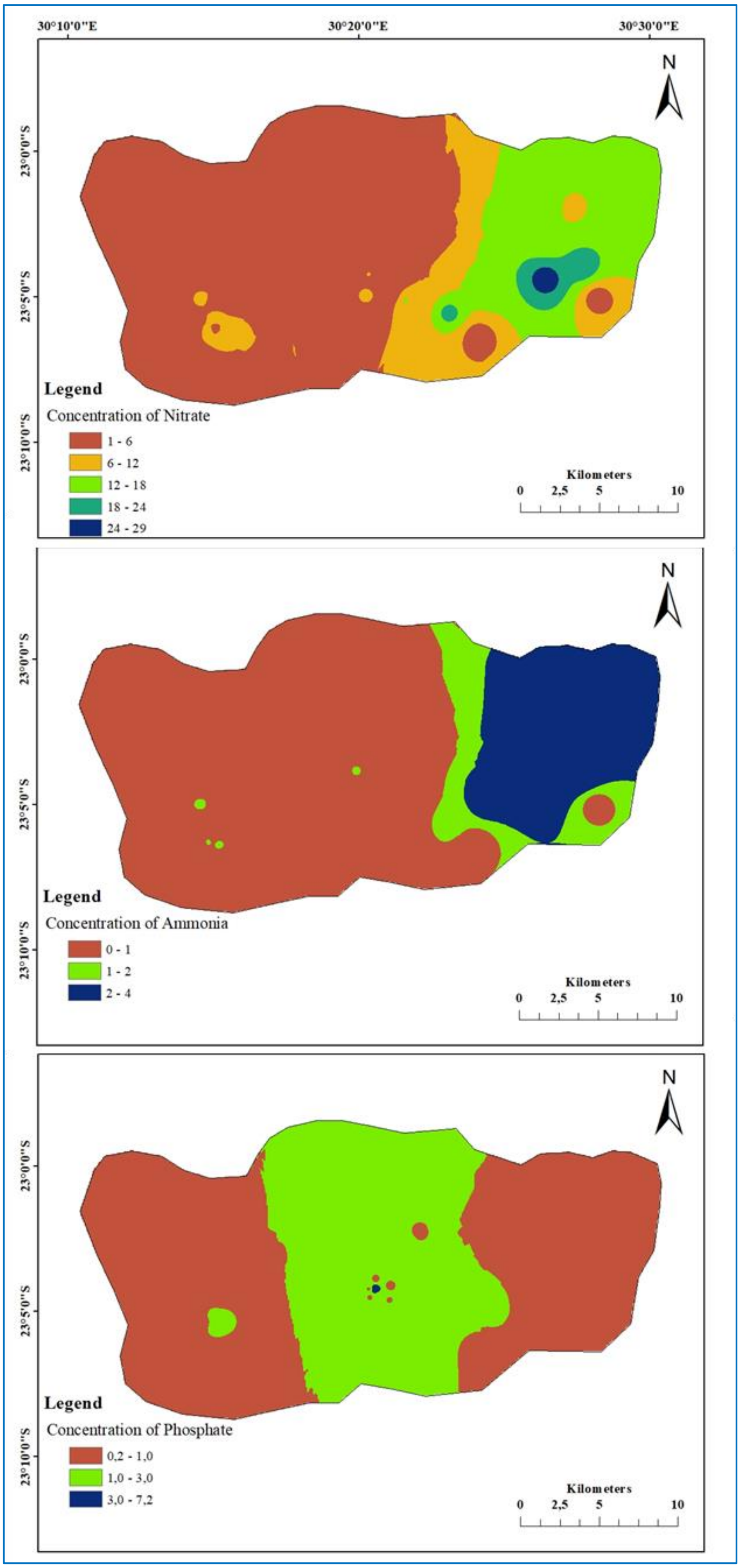

Figure 5. Spatial distribution of NO_3, NH_4 and PO_4 (mg/l) in the study area

5.4.2.1 Chromium (Cr)

Cr is a low mobility element especially, under moderately oxidizing and reducing conditions and near neutral pH (Machender et al. 2011). Chromium in groundwater ranges from 23 µg/l to 44 µg/l with an average of 34 µg/l. In the study region, the Cr concentration in groundwater is less than the WHO (2011) and DWAF (2015) recommended limit for drinking.

Figure 4 illustrates that Cr distribution does not show a specific trend and few pockets have high concentration. Natural source of chromium is chromite ore, mafic minerals, and minor quantities in Fe ores. Chromium and its compounds are mostly used in the paints, dyes, explosives, ceramics, and paper. Drinking water with high chromium causes nausea, skin ulcers, carcinogenesis gastrointestinal and lung cancer in consumers.

5.4.2.2 Zinc (Zn)

Zinc enters groundwater through geogenic processes and anthropogenic activities such as industrial activities, application of fertilizers and agrochemicals (Vetrimurugan et al.2017).

The concentrations of Zn in the groundwater of the study area is between below detection limit (BDL) and 813 µg/l with a mean and standard deviation of 106 µg/l and 224 µg/l, respectively. Zn concentration in groundwater is within the WHO (2011) and DWAF (2015) drinking water standards. The spatial pattern of Zn concentration in the groundwater suggests that high concentration is present in the upstream region (Figure 5) this may be due to the influence of weathering of parent material and the application of fertilizers containing Zn in this part of the study area.

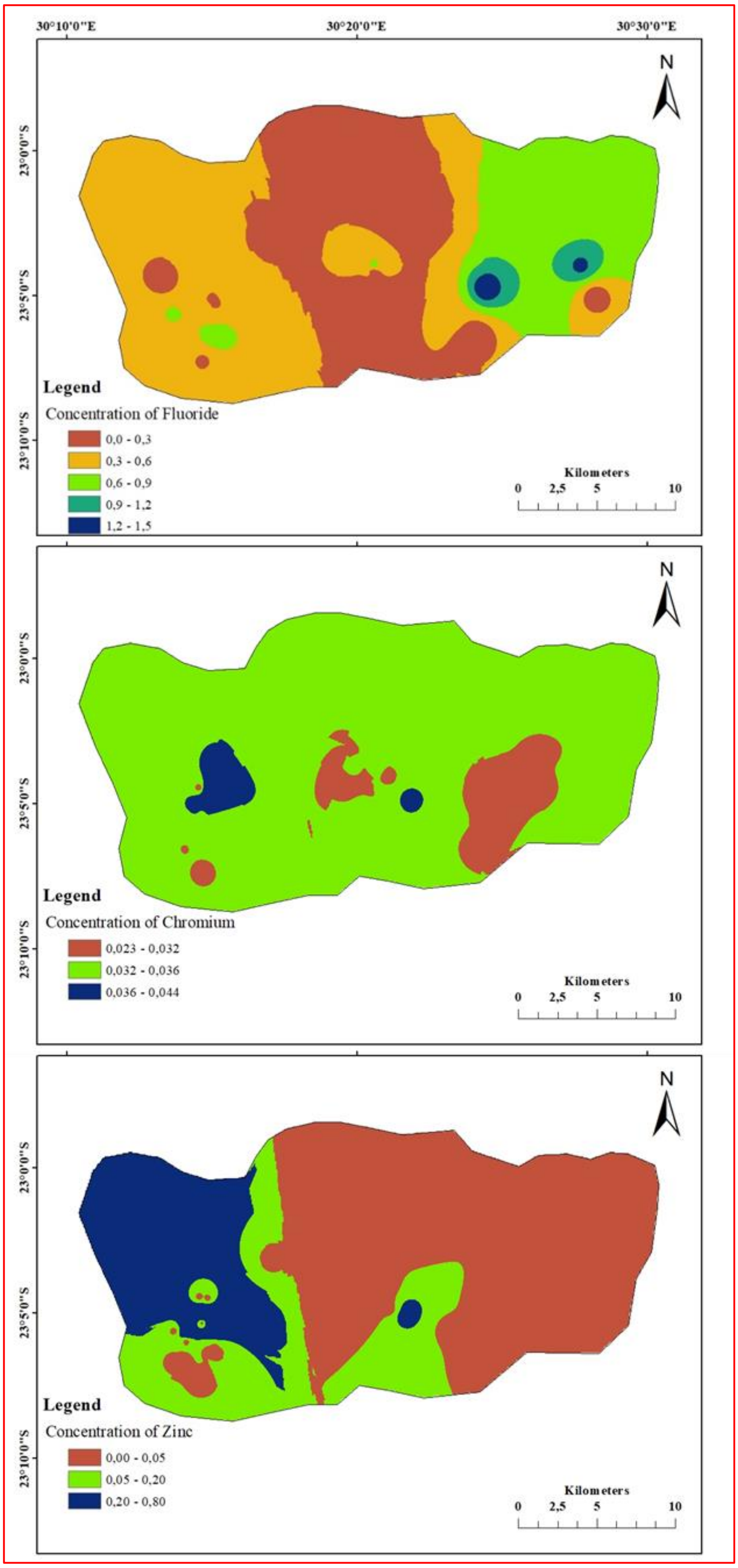

Figure 6. Spatial distribution of F, Cr and Zn (mg/l) in the study area

5.4.2.3 Lead (Pb)

All the groundwater samples in the study area have high Pb concentration, which exceeded the drinking water standards recommended by both WHO (2011) and DWAF (2015). Concentration of Pb ranges from 68 to 418 µg/l and the average and standard deviations are 196 µg/l and 70 µg/l, respectively. High Pb content is also noticed in river water. High Pb content in the drinking water causes serious health issues for consumers such as lethargy, anaemia, abdominal pain, paralysis in the muscles, etc. The spatial distribution indicates that higher values are noticed in the western region in addition with few hot spots in the downstream (Figure 7).

The geogenic sources for Pb are galena (lead sulphide), cerussite (lead carbonate) and anglesite (lead sulphate). Further, Pb is used in many industries and also existed in batteries, paints, and gasoline. Erosion of pipe network and water distribution pipes also lead to high Pb content in water.

5.4.2.4 Boron

Boron may be toxic in plants when it is in high concentration. Boron can damage crops if its concentration in water exceeds 2 mg/l (Driscoll et al. 2004). The concentration of boron in the groundwater varies from BDL to 92 µg/l with a mean value of 12 µg/l. Boron is detected only in 15 wells and it is BDL in the remaining wells. Groundwater boron concentration is within the WHO (2011) and DWAF (2015) drinking water standards and is recommended for drinking.

The spatial distribution of boron concentration shows that it is present in the upstream and southern regions only (Figure 7). Naturally, boron occurrence in groundwater resulted from rocks and soils containing borates and borosilicates. Anthropogenic sources include industrial air emissions, fertilizer and herbicide application, and industrial and municipal wastes.

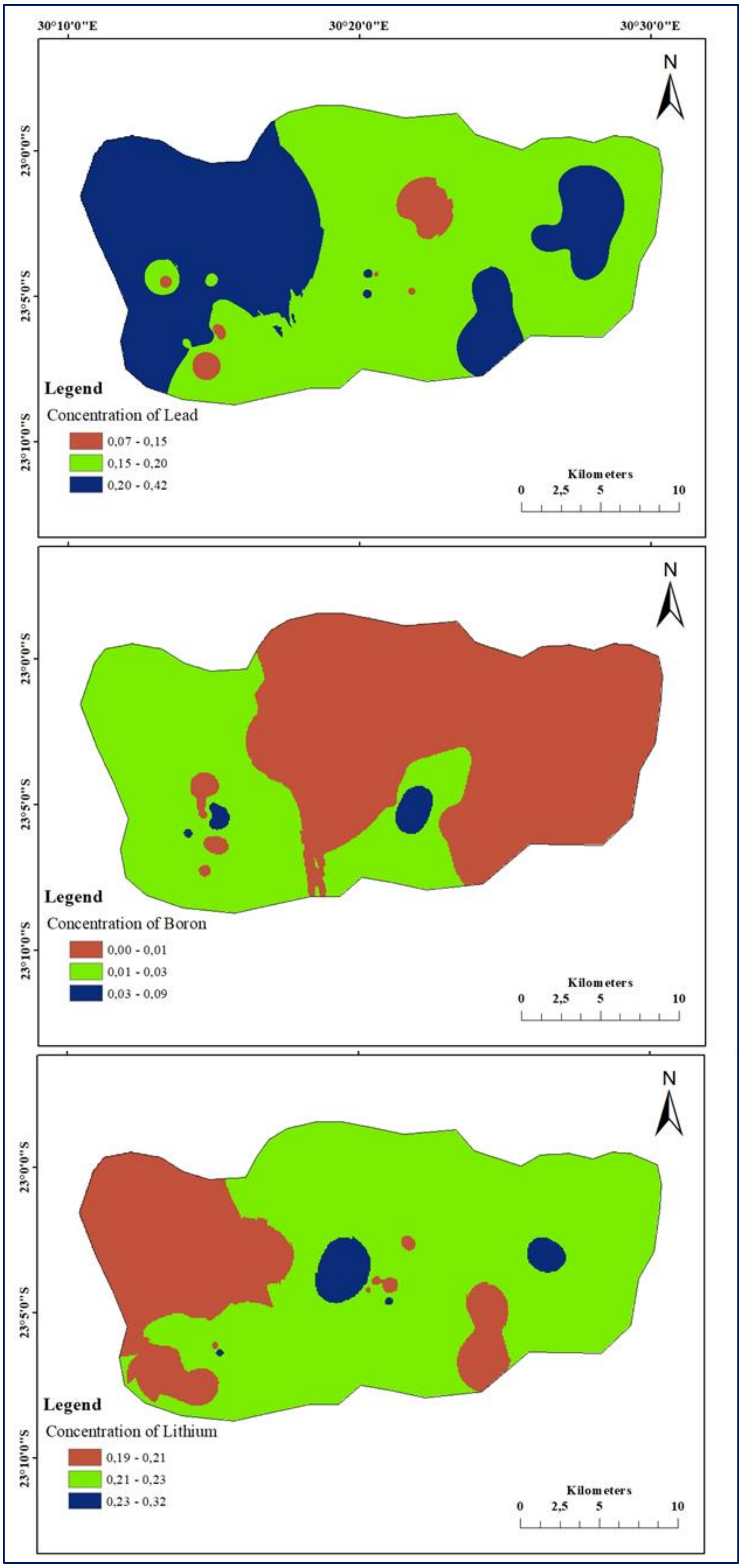

Figure 7. Spatial distribution of Pb, B and Li (mg/l) in the study area

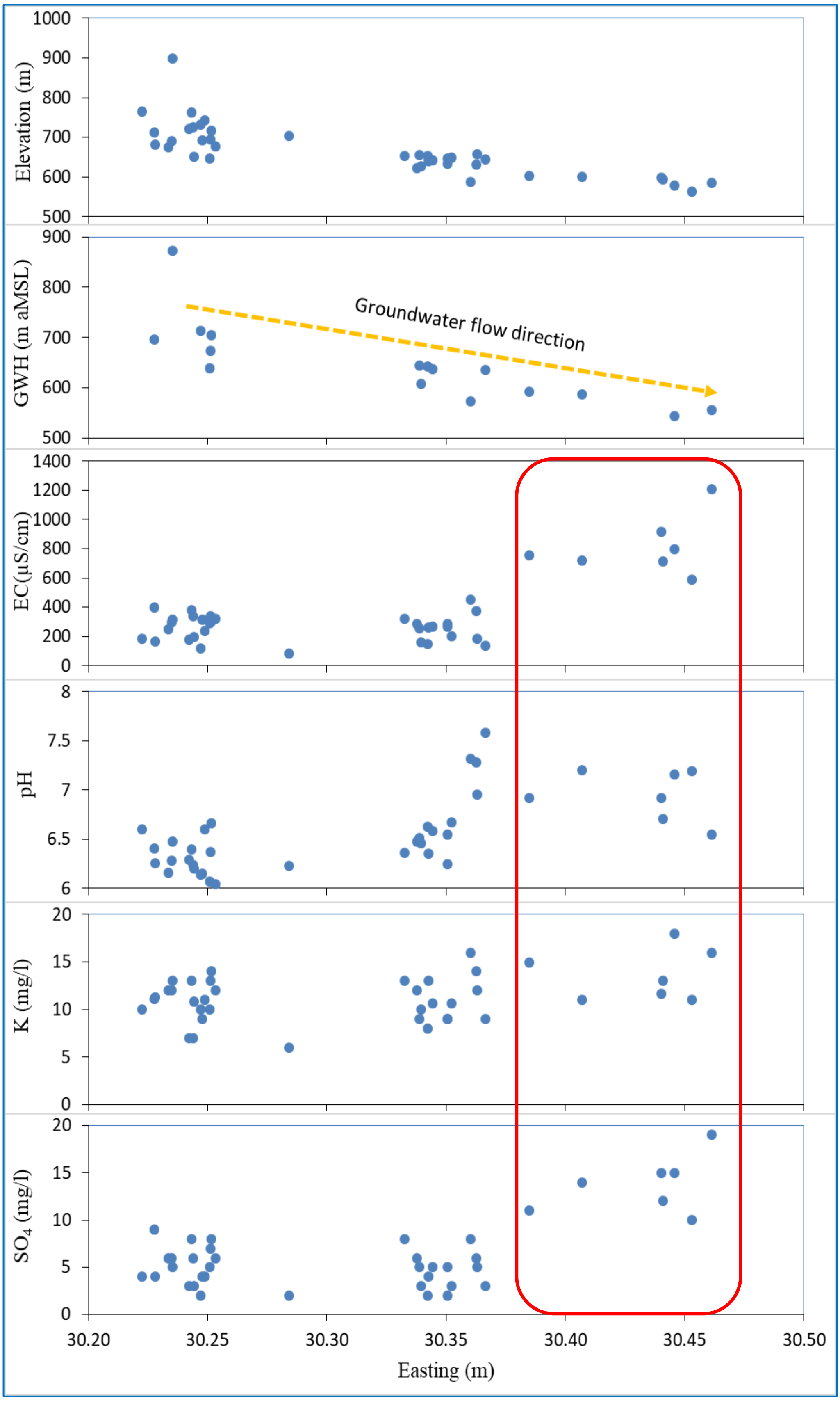

Figure 8. Relation between groundwater flow direction and selected parameters

5.4.2.5 Lithium

The concentration of lithium in the study area ranges from 185 µg/l to 322 µg/l and the average value is 218 µg/l. The spatial distribution pattern shows that lowest value is recorded in the upstream region and high values are noticed in few pockets (Figure 7). Lithium concentration in groundwater is generally low while it is observed high in seawater. As a result, lithium is often used as a tracer to differentiate the origin of salinity in the coastal groundwaters (Vetrimurugan et al. 2017).

5.4.2.6 Silica

In this study, silica varied from 1.0 µg/l to 9.0 µg/l with an average value of 5.8 µg/l. Silica in groundwater is derived from water-rock interaction mainly from weathering of phyllosilicates. Usually, the concentration of silica in groundwater range from 1 mg/l to 30 mg/l.

5.4.3 Relation between nutrients and trace metals distributions and groundwater flow direction

Figures 8 and 9 explains the occurrence and distribution of nutrients and trace metals in the groundwater flow direction. Groundwater flow is from west to east in the study area and justified by the elevation and groundwater head (m above mean sea level (m amsl)) in figure 6. EC values indicate that it is mostly constant until the centre of the study area, but a sudden enrichment is noticed in the downstream. Similar trends are found in the distribution of sulphate, nitrate, and ammonium concentrations. In contrast, pH and potassium behaved differently and they do not show abrupt variations with groundwater flow. The distribution of silica and fluoride are mostly similar, which are increasing with flow direction. However, the enrichment pattern does not comply with that of EC. In the case of trace metals, there is a decreasing trend in the flow direction especially in the case of B, Pb and Zn (Figure 8). In the eastern region, B and Pb are absent in the groundwater. However, there is no change in the concentration of Li, Cr, and phosphate in the groundwater flow direction.

5.4.4 Source of contaminations

The Luvuvhu catchment is an agricultural area and produces huge amount of variety of fruits and vegetables. Major land use activities in this area include subsistence, commercial agriculture, commercial forestry plantation and settlement areas. As the study region is covered by mostly agricultural farms and residential pockets, the nutrients and trace metals are likely originated from these sources. To assess the source of groundwater contamination, nitrate is plotted against all the variables. Figure 9 shows that nitrate has significant positive correlation with EC, sulphate, and ammonium in the groundwater. Likewise, fluoride also shows moderate positive correlation with nitrate. In addition, groundwater with high potassium and silica also has high nitrate concentration in the study region. But, pH, DO and phosphate do not show specific trend with nitrate and mostly constant. Positive relation between nitrate, EC, sulphate and ammonium implies that groundwater quality is affected by the surface contamination sources mostly from irrigation return flow, fertilizer applications and organic manure. However, groundwater with high silica and fluoride also has high nitrate, which justify that wastewater infiltration from surface should have likely triggered the mineral dissolution in the vadose zone and resulted in high concentrations of these elements in the aquifer.

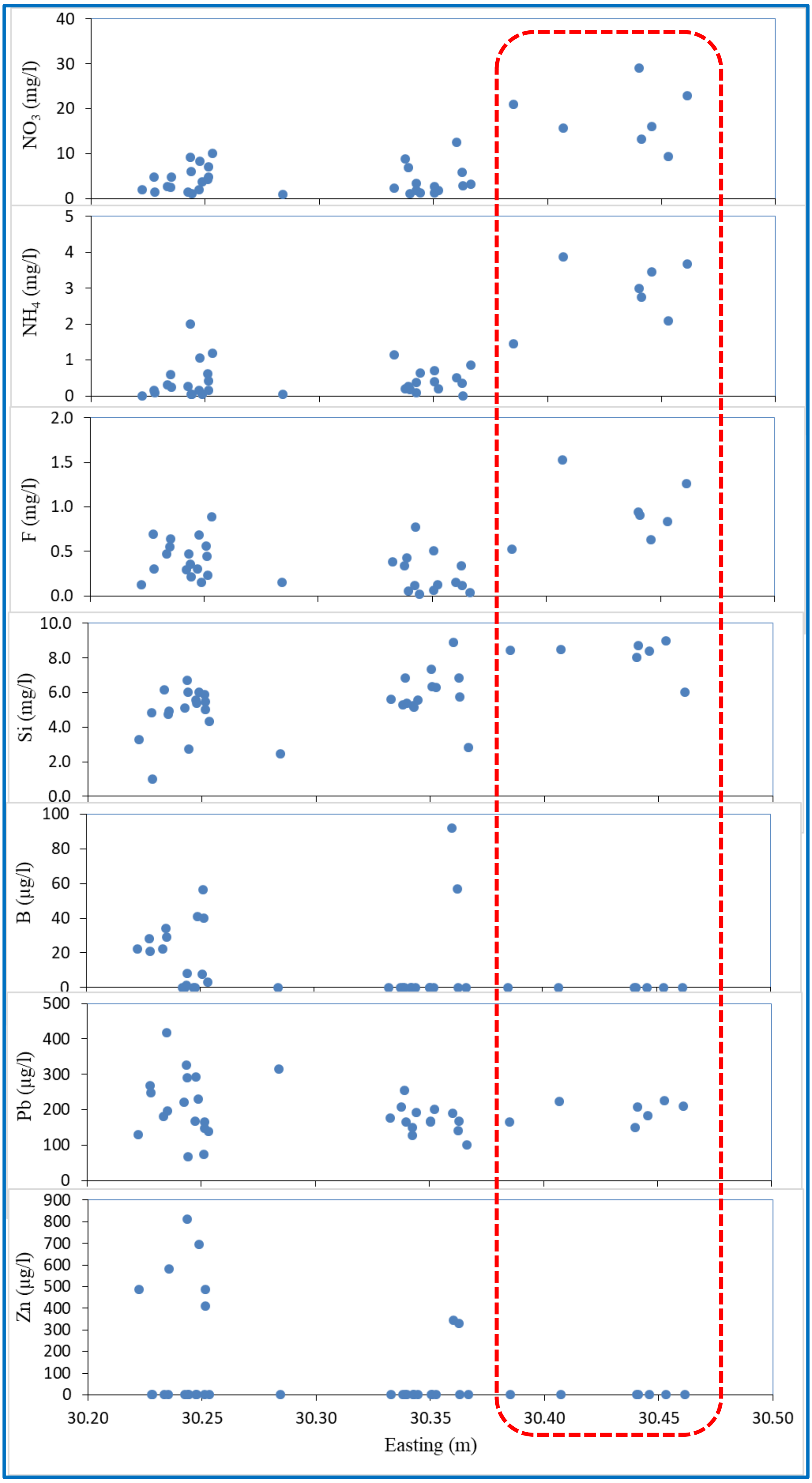

Figure 9. Relation between groundwater flow direction and selected variables

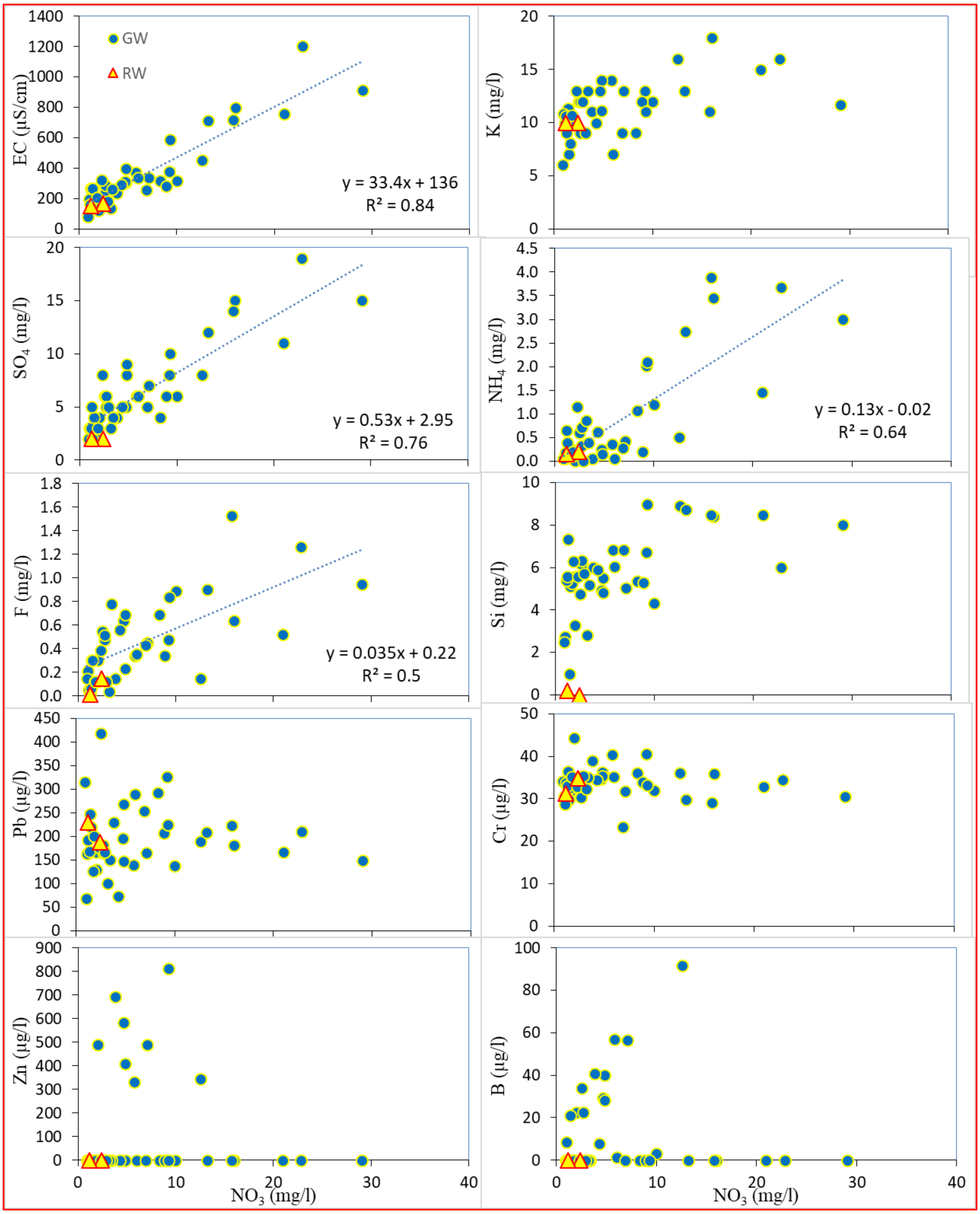

Figure 10. Relation between NO_3 and other variables in groundwater and river water (RW)

Figures 8, 9 and 10 illustrates that trace metals are decreasing from upstream to downstream. Further, these are not correlating with nitrate and high concentrations are recorded at low nitrate. Hence, most of the metals are likely to be derived from mineral weathering. However, boron concentration in few wells shows positive correlation with nitrate, which seems to be caused by the mixed sources namely natural sources and irrigational activities.

6. Conclusion

Occurrence and distribution of nutrients and trace metals content in the groundwater were studied in the intensively irrigated area to understand the influences of agricultural activities on groundwater contamination. The major outcome of this study is as follows:

i. Groundwater is mostly acidic in nature; however, slightly neutral to alkaline in the downstream region. The average EC (358 µS/cm) and TDS (233 mg/l) suggested that the groundwater is less mineralised and fresh.
ii. Drinking water suitability assessment suggests that pH, potassium and lead exceeded WHO and DWAF standard limits for drinking water in 51%, 31% and 100% of the groundwater samples, respectively, which are not suitable for drinking purposes.
iii. The spatial distribution of pH, EC, TDS and nutrients illustrate that higher values are noticed in the downstream areas.
iv. Occurrence and distribution of trace metals (Li, Pb, Zn, B and Cr) in the groundwater suggested that these are not uniformly distributed in the study area.
v. The relationship between nutrients and trace metal distributions and groundwater flow direction revealed that EC, sulphate, nitrate and ammonium

concentrations remained constant up to the central part of the study area. However, a sudden enrichment was noticed on the downstream part of the area. Likewise, silica and fluoride show increasing trend with flow direction. Trace metals (B, Pb and Zn) express a decreasing trend in the flow direction. But, pH, K, Li, Cr and PO_4 do not show abrupt variations with groundwater flow direction.

vi. Positive relation between NO_3, EC, SO_4 and NH_4 implies that groundwater quality is affected by the surface contamination sources mostly irrigation return flow, fertilizer application and organic manure.

vii. However, groundwater with higher nitrate also show higher concentration of silica and fluoride, which justify that recharge wastewater from surface likely triggered the mineral dissolution in the vadose zone and resulted in high concentrations of these elements in the aquifer.

viii. Trace metals does not correlate with NO_3; hence, most of the metals are likely to be derived from the mineral weathering. However, boron concentration in few wells shows positive correlation with nitrate, which seems to be caused by the mixed sources (natural sources and irrigational activities).

This study highlighted that groundwater quality monitoring is an important task for sustainable groundwater management in the study area.

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THEMATIC ISSUE

Occurrence and distribution of nutrients and trace metals in groundwater in an intensively irrigated region, Luvuvhu catchment, South Africa

Madondo T. Patience[1] · Vetrimurugan Elumalai[1] · N. Rajmohan[2] · Peiyue Li[3]

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Abstract

Agricultural activities are often associated with contamination of water, which resulted in high concentration of nutrients and trace metals in the shallow aquifer. Occurrence and distribution of nutrients and trace metals in the groundwater of intensively irrigated region of Luvuvhu catchment were carried out to determine the status of groundwater quality and its suitability for drinking. Groundwater samples were collected and analysed for physio-chemical parameters. The results suggest that the concentration of nutrients and trace metals in the groundwater are below the permissible limit of drinking water standards recommended by the World Health Organization and South African standards except pH, K, and Pb. Low pH (51%), potassium (31%), and lead (100%) restrict the groundwater usage for drinking. Relation between groundwater flow direction and EC, sulphate, nitrate, and ammonium contents indicate that it is mostly constant towards the center of the study area, but sudden enrichment is noticed in the downstream. Silica and fluoride have increased along with the direction of groundwater flow. Trace metals (B, Pb, and Zn) show decreasing trend in the flow direction. However, pH, K, Li, Cr, and phosphate concentrations do not show significant variation along the flow direction. Positive relation between nitrate, EC, sulphate, and ammonium implies that groundwater quality is affected by the surface contamination sources, and mostly from irrigation return flow, through the application of fertilizers and organic manures. However, groundwater with high silica and fluoride also has high nitrate, which justify that wastewater infiltration from surface has triggered the mineral dissolution in the vadose. Trace metals does not correlate with nitrate. High concentrations of trace metals are recorded with low nitrate, which implies that metals are derived from mineral weathering. However, boron concentrations in few wells show positive relation with nitrate, which justified the impact of natural sources and irrigational activities.

Keywords Nutrients · Trace metals · Luvuvhu catchment · South Africa

Introduction

Groundwater has always been considered a major source of freshwater reservoirs and it provides water for different human needs such as drinking, domestic, agriculture, and industrial usage (Vetrimurugan and Elango 2014; Agca et al. 2014; Barzegar et al. 2017; Chidambaram et al. 2018; Heydarirad et al. 2019; Zhou et al. 2020). Water availability, accessibility, and quality become more complicated worldwide in recent days due to climate change, natural, and man-made activities. The groundwater chemistry is largely influenced by various natural and anthropogenic factors. Natural factors, namely, temperature, pressure, rock types, soil formations, residence time, infiltration rate, etc. determine the water chemistry and quality (DWA 2010; Atikul et al. 2016; Magesh et al. 2017; Mthembu et al. 2020; Busico et al.

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✉ Vetrimurugan Elumalai
evetrimurugan@yahoo.co.in; ElumalaiV@unizulu.ac.za

1 Department of Hydrology, University of Zululand, Kwadlangezwa 3886, South Africa

2 Water Research Center, King Abdulaziz University (KAU), Jeddah 21598, Saudi Arabia

3 School of Water and Environment, Chang'an University, No. 126 Yanta Road, Xi'an 710054, Shaanxi, China