University of Venda

SCHOOL OF ENVIRONMENTAL SCIENCES
DEPARTMENT OF HYDROLOGY AND WATER RESOURCES

Trace element concentrations in geothermal springs and their impact on soil and vegetation in Siloam and Tshipise

By

Durowoju Olatunde Samod

Student No: 11634830

Supervisor: **Prof J.O. Odiyo**

Co-Supervisor: **Prof G.E. Ekosse**

A master’s dissertation submitted to the Department of Hydrology and Water Resources in fulfilment of the requirements of masters of environmental sciences

August, 2015

DECLARATION

I, Durowoju Olatunde Samod, hereby declare that this dissertation for the Master in Environmental Sciences degree at the University of Venda, hereby submitted by me, has not been previously submitted for a degree at this or any other institution. This is my work in design and execution, and all reference materials contained herein have been duly acknowledged.

Signature ____________________ Date: _________________

DEDICATION

This work is dedicated to God who is the beginning and the end.

This work is also dedicated to my parents, for their endless love, support and encouragement.

ACKNOWLEDGEMENTS

I would like to express my gratitude to Professor J.O. Odiyo and Professor G.E. Ekosse for supervising this M. Sc. dissertation. Their pieces of advice and commitment were most useful throughout the sampling, laboratory analysis and the writing of this work. They did not only supervise me but they continue to mentor and groom me to become the best in what I do.

I am sincerely indebted to Dr (Mrs) E.O. Popoola for her untiring attention to my academic pursuits from my undergraduate studies and laying the foundation for taking up my master's degree studies at the University of Venda. I wish to say a big thank you for her motherly advice and motivation towards my achievement in life.

I sincerely thank National Research Foundation (NRF), Pretoria and Research and Publications Committee of University of Venda for funding this research project. Their contributions have really propelled the completion of this project.

I would also like to thank the staff of the Department of Hydrology and Water Resources of University of Venda for not neglecting me and standing by me like a family from the beginning of this research.

My profound gratitude goes to the Agricultural Research Council (ARC) Pretoria where the samples were analysed after pretreatment at the University of Venda. I am also deeply indebted to Dr Diko, Mr T.R. Nkuna and Mrs R. Makungo for their remarkable advice and moral support during the course of this research.

To my wonderful family, particularly my parents (Mr & Mrs Durowoju) for their love and support throughout my life. Thank you both for giving me strength to reach for the stars and chase my dreams. My brothers (Abiodun and Oluwasegun) and little sister (Olaide) deserve my wholehearted thanks as well.

The endless support of my sister Ibeh Oluebube Sally could not be overlooked. I appreciate her words of encouragement towards my educational career. No words could ever repay your priceless efforts and commitment towards this achievement. I love you and your family, thanks for being around.

I smoothly went through my studies along with my mates Salim Zahara, Eghosa Solomon, Ologundudu Oladipo, Alayande Doyinmola, Ibitola Oluwabukola, Osidele Olujimi, Nemapate

Ndivhuwo, Arrey Ivo, Bukalo Nenita, Molepo Joey, Ramulongo Sluu, Mulaudzi Gundo, Tshipalafhasi Lufuno, whose friendship and hospitality were so precious to me. They enabled me to bear the hardships of being away from home in so many ways.

The endless support of all my friends, especially Ihidero David, Taiwo Babajide, Adekunle Olaide are acknowledged. I appreciate their words of encouragement towards my educational career. I am saying, I love you all.

ABSTRACT

Siloam and Tshipise Springs are scalding geothermal springs geologically located within the Soutpansberg Group in the Limpopo Province of South Africa. These geothermal springs are associated with faults and impermeable dykes and are assumed to be of meteoric origin. The optimal use of a geothermal spring largely depends upon its physical and chemical properties as well as the geological controls at source and surrounding pathway to the surface. This study aimed at investigating trace element concentrations in these geothermal springs in order to quantify their impacts on neighbouring soil and vegetation. Impact on vegetation was assessed by incorporating seasonal variations of the trace element mobility from the geothermal springs to the vegetation (*Mangifera indica* at Siloam and *Acacia robusta* at Tshipise) via soil. The geothermal spring water, soil and vegetation samples at both sites were collected from May – July (winter) and September – November (summer), 2014. The soil samples were collected at 5 m intervals up to 20 m away from the geothermal spring in each of the sites. The bark and leaf parts of the vegetation were sampled. The control samples for water, soil and vegetation were obtained from Riverside residence at University of Venda, Thohoyandou, Limpopo Province, where there is non-geothermal source of water.

The temperature, electrical conductivity (EC), pH and total dissolved solid (TDS) of the geothermal spring water and control samples were determined *in situ* and in the laboratory. The water samples were acidified for major cations and trace elements determination. There were also non-acidified water samples for major anion analyses. The soil and vegetation samples were digested using microwave and hot block methods, respectively. Concentrations of arsenic (As), antimony (Sb), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), mercury (Hg), lanthanum (La), lead (Pb), lithium (Li), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), tin (Sn), strontium (Sr), tellurium (Te), thallium (Tl), titanium (Ti), tungsten (W), vanadium (V), and zinc (Zn) were determined by inductively coupled plasma – mass spectrometry (ICP-MS) (Agilent 7700 series). Concentrations of calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K) were analysed using inductively coupled plasma – optical emission spectrometry (ICP-OES) (X – Series 2) whereas the concentrations of chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-), phosphate (PO_4^{2-}), bicarbonate (HCO_3^-) and sulphate (SO_4^{2-}) were determined by ion chromatography (IC) (Dionex Model DX 500).

Results from this study revealed that the geothermal springs were rich in trace elements compared to that from non-geothermal source of water. The mineral elements present were mainly due to rock-water interaction in the deep aquifer at both sites. The geothermal spring water is not fit for drinking because it is particularly high in fluoride (F) having 6.66 and 5.97 mg/L at Siloam ; 6.72 and 7.28 mg/L at Tshipise for winter and summer, respectively. Also, high Nickel (Ni) with 462 µg/L and 868 µg/L: Lead (Pb) with 652 µg/L and 211 µg/L at Siloam and Tshipise respectively, for summer season. In addition, it is not suitable for irrigation owing to high sodium absorption ratio (SAR) values which were above the standard guidelines (<1) by South African Bureau of Standards (SABS) and World Health Organization (WHO) at both sites. In summer season, there were higher trace elements concentrations than in the winter season. The higher concentration values could be attributed to rainfall, which aids in the dissociation of rock particles, resulting in higher concentrations of these elements. Siloam spring water was more mineralised than Tshipise spring water, hence its neighbouring soils and vegetation possess more trace elements concentrations than the latter.

Owing to their high mineral elements content, the geothermal spring water flows across the soil, making it vulnerable to sorption of the trace elements. The trace elements present in the surrounding soil of the geothermal spring were as a result of geothermal water and soil pedogenesis. The geothermal water contaminates the surrounding soil with substantial quantity of trace elements, which decreases with the distance from the geothermal spring, making far distanced soil less-contaminated. High levels of Cr, Co, Ni, Cu, Zn and Pb at Siloam soil can be attributed to more minerals present in the spring, therefore making absorption by *Mangifera indica* inevitable. Soils at Tshipise are moderately concentrated owing to moderate trace elements concentrations from the geothermal spring water.

Generally, seasonal variations were observed in the parameters analysed in the geothermal spring water, surrounding soil and vegetation to ascertain the most favourable season in terms of the trace elements concentrations. There were higher concentrations of trace elements in the geothermal spring, particularly during the summer season, compared to the winter season; this leads to more contamination of the surrounding soils and vegetation. This study showed that geothermal spring has potential to enrich the neighbouring soils and vegetation with trace elements, which could result in contamination. It can be concluded that geothermal spring, despite its benefits to humans, also contaminates the surrounding surface soils with toxic trace elements. Soils are a platform for vegetation. Therefore, if the soil is contaminated by toxic elements, there are high possibilities that these trace elements are absorbed by the neighbouring vegetation, which is likely to affect human beings adversely.

TABLE OF CONTENT

Contents **pages**

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

AIDS – Acquired immune deficiency syndrome
As – Arsenic
B – Boron
Ba – Barium
Be – Beryllium
Bi – Bismuth
Cd – Cadmium
Co – Cobalt
Cr – Chromium
Cs – Caesium
Cu – Copper
DNHPD - Department of National Health and Population Development
DWAF – Department of Water Affairs and Forestry
EC – Electrical conductivity
EC – European Community
IC – Ion chromatography
ICP-MS – Inductively coupled plasma-mass spectrometer
ICP-OES – Inductively coupled plasma- optical emission spectrometer
IARC - International Agency for Research on Cancer
Hg – Mercury
La – Lanthanum
Li – Lithium
MCL – Maximum contamination level
Mn – Manganese
Mo – Molybdenum
NHMRC – National Health and Medical Research Council
NMED – New Mexico Environment Department
Ni – Nickel
Pb – Lead
Pt – Platinum
QA – Quality Assurance
QC – Quality Control

Rb – Rubidium

SAR – Sodium absorption ratio

SABS – South African Bureau of Standards

Sb – Antimony

Se – Selenium

Sn – Tin

Sr – Strontium

TDS – Total Dissolved Solids

Te – Tellurium

Ti – Titanium

Tl – Thallium

U – Uranium

USEPA – United State Environmental Protection Agency

V – Vanadium

W – Tungsten

WHO – World Health Organisation

Zn – Zinc

LIST OF UNITS AND SYMBOLS

° - Degree

> - Greater than

<- Less than

µg/L – Microgram per litre

µS/cm – Mirco-Siemen per centimetre

mg/Kg – Milligram per kilogram

mg/L – Milligram per litre

mS/cm – Micro-Siemen per centimetre

ppb – Part per billion

ppm – Part per million

rpm – Revolution per minute

% - Percentage

CHAPTER ONE

INTRODUCTION

1.1 Background of the research

Hot water issuing from the earth's surface has been a subject of admiration since the dawn of mankind. Ancient civilizations revered geothermal springs because they were believed to have supernatural and healing powers (La Moreaux and Tanner, 2001). Geothermal springs develop when surface water percolates into the earth and encounters hot volcanic masses of rock. The water is heated and returns along faults, to the surface of the earth, as hot water. The same process occurs when rainwater penetrates the ground, infiltrate to great depths where it becomes heated, and then returns to the earth's surface while it is still hot (Higgins and Higgins, 1996).

Trace elements are also known as potentially toxic elements, trace metals, heavy metals, micronutrients, and minor elements in the environment (Alloway, 1995). Heavy metals are natural components of the earth's crust. The natural occurrence of heavy metals varies between rock types and certain bed-rocks. The rock types provide exceptionally high metal concentrations to overlying soils. Soils are of enormous environmental importance, being the media that support virtually all plant life, hence their potential for environmental pollution requires attention (Scancar *et al*., 2003). While soils are important receptacles for heavy metals, they can also release them into the ecosystem. It is therefore important to understand the content, chemistry and geology of heavy metals in geothermal water, soil and vegetation as well as the chemical forms.

People have used water from geothermal springs for different purposes for thousands of years (Olivier *et al*., 2011). Documentary and oral history reveal that geothermal springs were used for bathing, medicinal, religious, hygienic and social purposes across world, for instance, India, Crete, Egypt, Turkey, Japan, Brazil and Canada (van Vuuren, 1990; Lund, 2000). In addition to the increasing popularity of spas and the growing importance attached to the 'natural' health industry (Smith and Puczkò, 2009), geothermal springs are increasingly being used for power generation, industrial processing, agriculture, aquaculture, bottled water and the extraction of rare elements (Vimmerstedt, 1998; Lund, 2000; Hellman and Ramsey, 2004; Petraccia *et al.,* 2005).

Several researchers have suggested that geothermal waters are useful tools in the treatment of illnesses such as functional dyspepsia, irritable bowel syndrome and functional disorders of the biliary tract (Garzon and Eisenberg, 1998; Bonfante *et al*., 1999; Bortolotti *et al*., 1999; Capurso *et al*., 1999; Serio and Fraioli, 1999; Fraioli *et al*., 2001; Bertoni *et al*., 2002; Grassi *et al*., 2002;

Fioravanti *et al*., 2003 and Petraccia *et al*., 2005), since carbonated water stimulate the secretion and motility of the digestive tract (Schoppen *et al.,* 2004; Gasbarrini *et al.,* 2006). Furthermore, salt-rich mineral waters enhance the conversion of cholesterol into bile acids and their subsequent secretion (Capurso *et al*., 1999; Grassi *et al*., 2002). Spring mineral therapy with sulphurous water can provide beneficial effects in chronic inflammatory disorders with an immunologic pathogenesis by inhibiting the immune response at a local level (Grassi *et al*., 2002).

Spring mineral waters have antioxidant and hypocholesterolaemic activity. These may affect calcium metabolism (Toussaint *et al*., 1986). For example, sulphurous mineral water was found to have anti-oxidant properties and a positive effect on the oxidative defence mechanism on both rabbits and rats, respectively (Grassi *et al*., 2002). Magnesic-sulphate-sulfurous spring mineral water has been demonstrated as having a very good hypocholesterolaemic activity and a protective effect against oxidative lipid damage (Grassi *et al*., 2002). The oral intake of water containing calcium increases serum calcium and inhibits intact parathyroid hormone secretion (Cantalamessa and Nasuti, 2003). However, results vary depending on the chemistry of the water (Nerbrand *et al*., 2003).

Limpopo Province in South Africa is richly-endowed with geothermal springs, with about 24 geothermal springs. Some of these have been developed for recreational and touristic purposes, while water from some of them is bottled and sold for therapeutic purposes (Olivier *et al*., 2008). In some cases, a geothermal spring is the sole source of water for the population. Few geothermal springs remain in private hands for exclusive use by the land owner, like Siloam Spring located at Siloam village. Previous works revealed that the Siloam and Tshipise springs are regarded as the hottest springs in the country with temperatures of 64 °C and 58 °C, respectively (Olivier *et al*., 2008).

This study focuses on trace elements concentrations in Siloam and Tshipise springs and their impact on the environmental media; that is, the soil and the vegetation around the springs as well as the seasonal variations. The results were compared to that of a non-geothermal spring, probably a borehole around the location which will serve as a control site. These two springs are regarded as scalding springs because of their high temperatures, which might result in elevated concentrations of trace elements in the springs (Kent, 1949). Previous study by Olivier *et al*. (2011) revealed that the concentrations of some trace elements in Siloam and Tshipise springs are high, compared to the WHO (2000), DWAF (1996) and SABS (1999) standards.

Some of the trace elements such as iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), cobalt (Co), molybdenum (Mo), vanadium (V) and nickel (Ni) are essential for the growth of organisms. Other trace elements: cadmium (Cd), lead (Pb), uranium (U), thallium (Tl), chromium (Cr), silver (Ag), mercury (Hg), arsenic (As) and selenium (Se) are toxic to organisms. It has been established that these trace elements are present in these springs, hence the long-term ingestion of water from these sources may be hazardous to human health (Olivier *et al*., 2011).

1.2 Statement of problem

Geothermal springs are usually mineralized depending on the characteristics of the geological formations associated with the circulating groundwater (Todd, 1980). A number of studies have found that geothermal water may contain toxic elements such as arsenic (As) and mercury (Hg) (Manda and Suzuki, 2002; Romero *et al*., 2003; Churchill and Clinkenbeard, 2005), radio-active elements such as uranium (U), thorium (Th) and Radon (Rn) (Kempster *et al.,* 1997; Baradács *et al.,* 2001) and pathogenic organisms such as the meningitis causing *Naegleria fowleri* (Sugita *et al.,* 1999; Izumiyama *et al.,* 2003; Craun *et al.,* 2005) and *Legionella pneumonia* (Miyamoto *et al.,* 1997).

A field survey on Siloam Spring at Siloam Village revealed that people fetch water for domestic uses in addition to the water being channelled towards some vegetation in the neighbourhood. Tshipise Spring is located within the Honnet Nature Reserve, approximately 36 km from Musina and is a popular holiday resort. The spring's water is used for irrigation in subsistence farming (at Siloam), irrigation of flowers, grasses and trees (at Tshipise) and serves as the source of water for the pool at the resort. Thus, trace elements are transferred from the geothermal spring across the soil to the vegetation and have potential adverse effects on humans when the concentration is significantly high.

The mango tree (*Mangifera indica*) is the dominant plant available in the neighbourhood of Siloam geothermal spring whereas Enkeldoring (*Acacia robusta*) is the most common plant around Forever Resort, where Tshipise geothermal spring is located. *Mangifera indica* and *Acacia robusta* can be cultivated under conditions which vary from very hot and humid to cool and dry, to very hot and arid with low maintenance (Ojekunle *et al*., 2014). Thus, the geothermal spring water has the potential to contaminate the surrounding soils and vegetation with trace elements.

1.3 Motivation

Weathering processes of reactive minerals in surrounding and mainly acidic rocks mobilise heavy metals and toxic elements (Cu, As) from primary minerals and form secondary constituents (mainly iron hydroxides, copper-oxides and carbonates), causing contamination of technogenous sediments, soils and surface water, drainage water as well as groundwater (Younger *et al.,* 2002). Heavy metal contamination is a major environmental concern due to their toxicity, carcinogenicity and mutagenicity even at low concentrations. These mineral elements can cause damage to organs of human body (Ifegwu and Anyakora, 2012).

This study focuses on quantitative analysis of cations, anions and trace element concentrations which are obtained from the increased dissolution of the rock as a result of the high temperature. A study by Odiyo and Makungo (2012) reported that geochemical dissolution of the rock increases with temperature. The areas of this research (Siloam and Tshipise) are rural settlements in which the people have little or no idea of the effects of the toxicity of these trace elements in the environment. Spring water is used for various domestic purposes: as a source of water for the swimming pool and even for irrigation purposes as indicated earlier but with no clear understanding of the potential health effects from mineral elements. It is therefore important to establish whether the geothermal spring contaminates the neighbouring soil and vegetation with toxic elements or not.

A number of studies have been carried out on the physicochemical parameters of geothermal springs in which these mineral elements compositions are stated. However, none has shown their impacts on the soil and vegetation (Kent, 1949; Olivier *et al.,* 2008; Mamba *et al.,* 2008; Olivier *et al.,* 2011; Tekere *et al.,* 2012). This study also investigates the present physicochemical parameters of the geothermal springs using a different methodology as compared to the last analysis carried out by Olivier *et al*. (2010). The study focuses on quantitative analysis of the trace elements concentrations in these geothermal springs' water and their impacts on soil and vegetation around the geothermal springs. Seasonal variation (particularly winter and summer seasons) of the trace elements mobility, were observed to ascertain if the chemical composition changes with season. The results obtained from this research will not only be of interest to the communities within the neighbourhood of the geothermal spring but also to higher authorities regulating water issues in the country.

1.4 Objectives

1.4.1 The main objective

The main objective of the study was to investigate trace element concentrations in geothermal springs in Siloam and Tshipise and non-geothermal source of water, as well as their impacts on soil and vegetation in relation to seasonal variations.

1.4.2 Specific objectives

- To determine the physico-chemical characteristics (pH, EC, TDS, temperature, major cations and anions) in the water from the geothermal springs and non-geothermal source, surface soil and vegetation;
- To determine the concentrations of trace elements in the geothermal spring water, surface soil and vegetation around Siloam and Tshipise springs;
- To determine the horizontal status of trace elements from the geothermal spring water to the surface soil at both sites;
- To probe correlations among parameters analysed in the geothermal spring water, the soil and the vegetation.

1.5 Research Questions

- What are the physico-chemical parameters in the geothermal springs' water, non-geothermal water, soil and vegetation?
- What are the concentrations of trace elements that are available in the geothermal springs' water, non-geothermal water, soil and vegetation?
- What is the horizontal status of trace elements from the geothermal spring water to the surface soil?
- Is there any increase or decrease in the concentration of trace elements in this order-spring water to the soil and to the vegetation or vice versa?

1.6 Hypotheses

The following are the hypotheses of this study:

- Trace element concentrations are much higher in geothermal springs compared to non-geothermal springs.
- The soil and vegetation accumulate some reasonable quantities of the mineral elements from the geothermal springs.
- Trace element concentration decreases with distance from the geothermal spring source.

- Geothermal springs contaminate the soil with toxic trace elements which is likely pose adverse effects on human beings.

1.7 Study Area

Tshipise and Siloam geothermal springs are located in the Limpopo Province of South Africa (Figure 1.1) and are of different surface geology but fall on the Soutpansberg Group. The geology determines the extent to which the reaction with the host rock proceeds (Figures 1.2 and 1.3), depending on the chemical composition of the rock and the rate at which water passes through the rock. The study areas are characterised with high temperature variations in different seasons of the year with temperature in winter ranging from 16ºC to 22ºC and summer ranging from 22ºC to 40ºC (Makungo, 2008). The mean annual rainfall of Nzhelele ranges from 350-400 mm per annum (Makungo et al, 2010). More than 80% of the rainfall occurs in the summer and only about 20% occurs in the winter (DWAF, 2001). Figure 1.1 shows clearly the position of the study area and the distance between Siloam and Tshipise springs, which is approximately 130 km apart and the Soutpansberg Mountain Range separates the two springs.

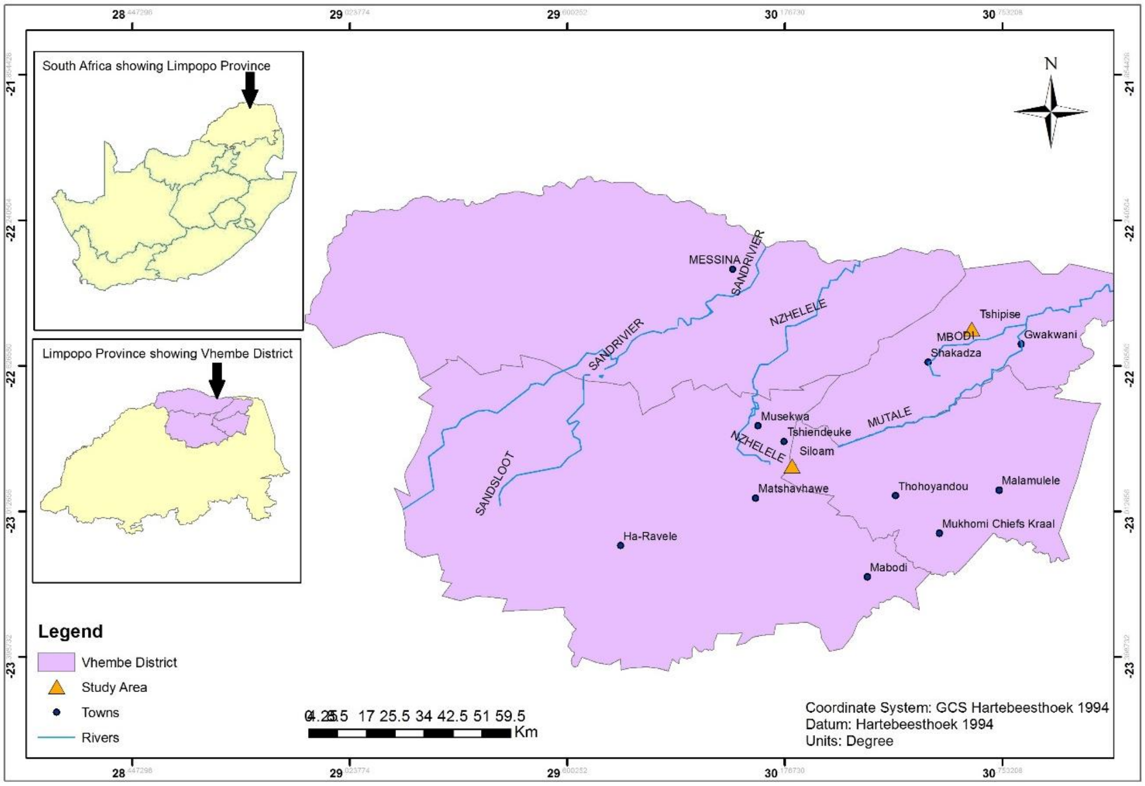


Figure 1.1: Map of Vhembe District showing Siloam and Tshipise geothermal springs, Limpopo Province, South Africa

1.7.1 Siloam Spring

The Siloam spring is found in Nzhelele Valley at Siloam Village which falls under the youngest Formation of the Soutpansberg Group, which is the Sibasa Formation. Siloam geothermal spring is located on the coordinate of 22° 36’ 05.48" S and 30° 10’ 23.01" E. It is dominated by basalt (Figure 1.2), which originated from the lava at the base of the Formation. It is responsible for the more undulating topography to the south of the Soutpansberg (Brandl, 1986). There are dark-red shale and sandstones that are fine, thinly-bedded sandstones. There is an interlayer of tuff, ignimbrite and chert and in places tuffaceous shale (Mundalamo, 2003). Various types of conglomerates are also available, such as argillaceous and arenaceous types. The mudstone and siltstone of Delvis Gully member also exist (Mundalamo, 2003). Siloam village is characterized by fractured aquifers of sandstone where groundwater occurs. The Siloam Spring is found on a private property at Siloam Village.

1.7.2 Tshipise Spring

Tshipise spring is found on the Leeward side of Soupansberg Mountain Range. The spring is underlain by volcanic rocks of the Letaba Formation at Karoo Super Group. Tshipise geothermal spring is on 22° 53’ 09.66" S and 30° 12’ 40.36" E of the equator. Tshipise is located close to the confluence of two faults: one is called the Tshipise Fault and the other is Bosbokpoort Fault (Johnson *et al*., 2006). The Letaba Formation immediately underlying the spring at Tshipise comprises mainly of basalt, arenite and marble (Figure 1.2). The spring also lies close to a dolerite intrusion, and to the contact between the Lebata Formation and the Gumbu Group of the Beit Bridge Complex, which underlies the spring at Moreson. The Gumbu Group comprises mainly calc-silicate rock and marble (Brandl, 1986). Tshipise geothermal spring is in a resort centre called Forever Resort on the way to Musina.

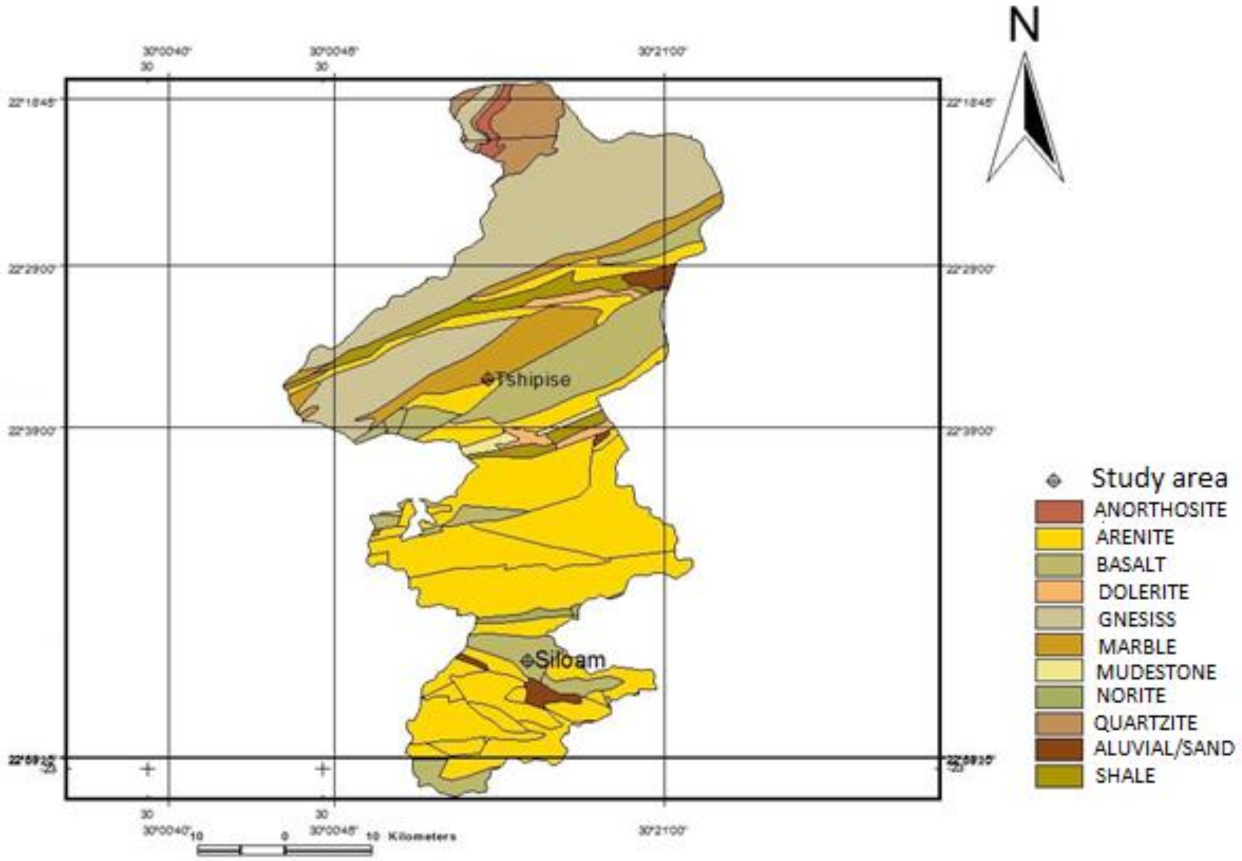


Figure 1.2: Geology of Siloam and Tshipise

CHAPTER TWO

LITERATURE REVIEW

2.1 Preamble

This chapter presents a concise review of the literature relating to geothermal springs with more emphasis on the trace element concentrations as well as their impacts on soil and vegetation. The general overview of geothermal springs in South Africa outlines the origin, benefits of the geothermal springs, physical and chemical properties as well as the trace elements migration from the spring water through the soil to the vegetation. The literature review also covered the chemistry of the geothermal springs and the geology associated with the springs.

2.2 Origin of geothermal springs

The origin of geothermal springs has been associated with volcanogenic activities (volcanic origin) and the impact of geothermal gradient on the percolating/infiltrating surface waters (meteoric origin) (La Moreaux and Tanner, 2001). These two processes are illustrated on Figure 2.1 and explained further in the proceeding sections.

2.2.1 Geothermal springs of volcanic origin

Geothermal springs occur in volcanic areas where reservoirs of molten or slowly cooling magma lie close to the surface and have heated the rocks above (Scheffel and Wernert, 1980). The water is heated as it flows through cracks in the rocks, and if the passage of the water to the surface is unobstructed, the heated water continuously bubbles up to the surface and so forms a geothermal spring (Scheffel and Wernert, 1980). The high temperature gradient near magma may cause water to be so heated that it boils or becomes superheated. If the water becomes so hot that it builds steam pressure and erupts in a jet above the surface of the Earth, it is called a geyser. Examples include crystal hot spring in Utah (USA), the Frying Pan Lake in Waimdigu volcanic rift valley (New Zealand), the geyser hot spring (Iceland) and Methane Peninsula (Greece) (Kevin *et al*., 2005).

2.2.2 Geothermal springs of meteoric origin

Geothermal springs from meteoric origin are formed due to the effect of geothermal gradient which is the rate of temperature increase with the depth of the rock (non-volcanic activity) (Press and Siever, 1986). The temperature increases with increasing depth in the earth. Cold water from rain, rivers or lakes may descend along a fault to a depth of several kilometres. This underground water is heated due to the geothermal gradient of 2˚C - 3˚C per 100 m (geothermal gradient)

(Press and Siever, 1986), which causes it to expand and rise up another fault and so create a convection system (Hoole, 2001; La Moeaux and Tanner, 2001). The temperature of the geothermal spring thus reflects the depth of penetration of the water and the rate at which it ascends to the surface (La Moreaux and Tanner, 2001; Grasby and Leptzik, 2002). Examples of such springs include Aachen (Germany), Lochinvar hot springs (Zambia), Ihimba hot springs (Uganda), Olympic hot spring (Washington, USA) and Hetling spring (UK).

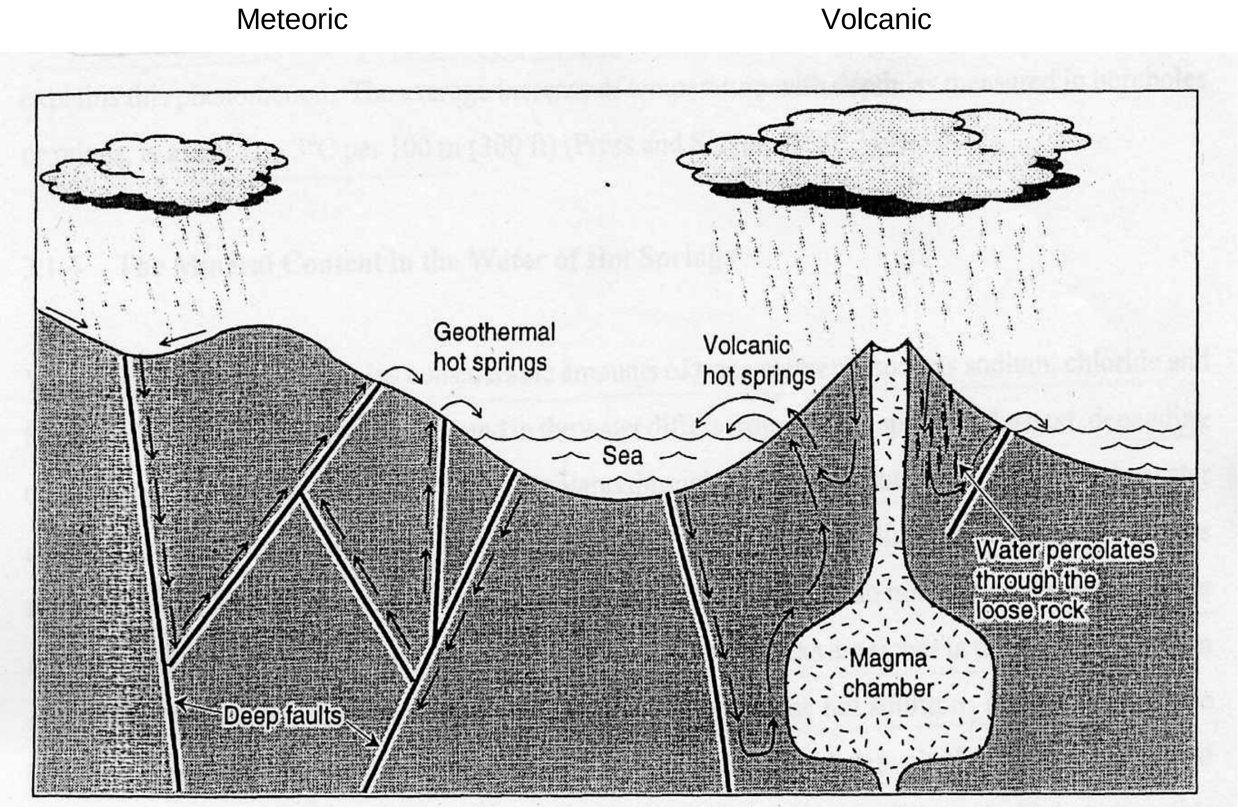


Figure 2.1: Diagrammatic representation of the origin of geothermal springs (Higgins and Higgins, 1996)

The source of water for geothermal springs in South Africa is meteoric rather than volcanic (Kent and Groeneveld, 1962; Gevers, 1963; Visser, 1989, Hoole, 2001), and the process is generally associated with faulting and shearing. Geological studies have also shown conclusively that the origin of each individual geothermal spring can be attributed to the local presence of deep geological structures such as folds, fractures, faults and dykes. These structures provide a means for the circulation to depth and the return of the heated waters to the surface (Olivier *et al*., 2010). Examples of such geological studies include Siloam spring and Tshipise spring. Water from geothermal springs generally originate from precipitation or rainfall, snowmelt or water seeps, then heated up by the magma close to the earth's surface. Heated water is much less dense than the rock that surrounds it, and thus it rises to the surface, in the form of a spring. The water is carried in conduits, through the water table, fractures and other passages where the water can flow (Watson, 1997).

Sufficient rain needs to fall in the catchment areas of the springs; therefore South African thermal springs are confined to areas with annual rainfall in excess of 254 mm (Witcher, 1981). Geothermal springs originate from a combination of special conditions. The four basic parameters for these conditions are:

- A heat source
- A recharge source
- A circulation framework or storage reservoir
- A discharge mechanism

The heat source is the most basic parameter because it is the one that distinguishes geothermal springs from non-geothermal springs (Witcher, 1981). As the hot water comes to the earth surface it dissolves away rocks and carries minerals in the created solution. Due to this dissolution, the water may become enriched in minerals. Elements that can be found in geothermal springs include: As, B, Cl, Si, S, Rn many others (Brock, 1994). Therefore a geothermal spring water can be considered as a "mineral spring", a spring that must have 400 ppm of dissolved solids in its waters (Mountain Nature, 2003).

2.3 Chemistry of geothermal spring

Different chemical reactions occur within geothermal waters, which are mostly associated with interactions between the water and the rock of the chambers in which it is located. Within the waters many other reactions occur, and these typically involve anions and/or metal cations/ trace elements (Hodder, 2005). As the rainwater falls in the recharge area, it first passes down through leaves, soil and other debris on the surface. The living animals in the debris and soil give off carbon dioxide and this is dissolved in the water and forms a weak carbonic acid (eqn. 1).

$$H_2O + CO_2 \longrightarrow H_2CO_3 \text{ ....eqn. 1}$$

This acidic water now moves further down in the Earth, through the different layers of chert, including the thick layers of novaculite. The novaculite and chert include the skeletons and spicules of radiolarians and graptolites, which are made of calcium. This calcium along with the rock exists in a form called calcium carbonate ($CaCO_3$). As the water passes through the chert formations, it dissolves some of the calcium carbonate (Olivier *et al*., 2010). The carbonic acid in the water reacts with the calcium carbonate to form soluble calcium bicarbonate (eqn 2).

$$H_2CO_3 + CaCO_3 \longrightarrow Ca(HCO_3)_2 \text{ ……………………..eqn. 2}$$

In this process, the carbonic acid is partially neutralized and the solution gradually becomes more alkaline. Calcium bicarbonate only exists as a solution. As this solution moves deeper into the earth, it heats up and dissolves some silica from the surrounding rock layers. The underground heat helps to make the calcium bicarbonate solution (water) more buoyant, and the broad cracks and faults across the face of the geothermal spring which give this solution an escape route to the surface. When the solution Ca (HCO_3)$_2$ reaches the surface, the dissolved carbon dioxide (CO_2) quickly escapes as shown in eqn. 3:

$$2Ca\,(HCO_3)_2 \longrightarrow 2CaCO_3 + 2H_2O + 2CO_2 \uparrow \text{ ………………eqn. 3}$$

It is important to note that calcium carbonate is formed from the release of carbon dioxide, not from the change in temperature from rising to the surface. Calcium carbonate is actually more soluble in cool water. The water remains in the aquifer for a sufficiently long time (hundreds to thousands of years) and the reactions are sufficiently slow for them to be used to calculate the temperature of the water. In effect, the ratios of the concentrations of the liberated cations (Ca^{2+}, Na^+, K^+) are temperature dependent. The solubility of silica is also temperature dependent, but this equilibrium is attained rather more rapidly than the dissolution of other silicate minerals (eqn. 4) (Hodder, 2005).

$$\underset{\text{Dissolved silica}}{2H_4SiO_4\,(aq)} \rightarrow \underset{\text{Quartz siliceous sinter}}{4H_2O + 2SiO_2} \text{ ....eqn. 4}$$

This reaction (eqn. 4) can be used as a geo-thermometer too. Any difference in temperatures obtained from the two geo-thermometers is related to the sampling of the water relative to the deep aquifer: waters that have moved away from the aquifer are likely to have lower temperatures derived from silica concentrations than temperatures derived from concentrations of Na, K and Ca. As the water rises to the surface it cools, and silica and other minerals are precipitated. This may help "cap" the aquifer, and prolong the geothermal system's existence. Water that does reach the surface through faults and fractures will cool further and produce the sinter mounds and terraces that are typical around geysers and hot springs (Hodder, 2005).

Hydrogen sulfide and other gases are dissolved in geothermal water that originates in the magma, including hydrogen chloride. Thus, chloride ion in geothermal waters can be at high concentrations. Both hydrogen sulfide ions (HS^-) and chloride ions (Cl^-) can form complexes with trace elements as shown in eqn. 5 below:

$$M^{2+} (aq) + nX^- (aq) \text{ --------- } M (X)_n^{2-n} (aq) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{eqn. 5}$$

Where X $^-$ anions such as Cl^-, SO_4^{2-}, HCO_3^{2-}, HS^- among others;

M - trace elements

Some of these trace elements may have been expelled from the magmas as gaseous sulfides and halides; others may have entered the geothermal water through their reactions with aquifer rocks (Hodder, 2005).

2.4 Benefits of geothermal springs

2.4.1 Religious and traditional benefits

Religious and traditional uses of geothermal springs have been an ancient practice across the world even before modern civilization. For instance, the American Indians used the geothermal springs for traditional rituals and as a neutral ground where different tribes could hunt, trade and bath and where warriors could travel and relax (Hoole, 2001). The Greeks usually attribute their religion to cleanliness. Therefore, they built their temples close to the geothermal springs so that the water reticulation system could bring water to the holy place (Virk *et al*., 1998). Africans were not exempted from these beliefs; geothermal springs found at the Gumara River in Ethiopia were discovered by Ethiopian saints; Qergos and Takla Haymanot. It was believed that saint Qergos, while flying in the sky, was attacked by eagles and his bones fell to the ground causing warm and healing water to rush out where they were dropped (Pankrust, 1990). Some of the sites have been declared heritage sites and are presently visited by both local and international tourists (Pankrust, 1990; Nguyen, 2007).

2.4.2 Medicinal benefits

Medicinal benefits and religious purposes of geothermal springs are interrelated and can be traced back to 2,500 years ago (La Moreaux and Tanner, 2001). Geothermal springs were believed to be a special kind of groundwater owing to its higher mineralization as well as trace elements, dissolved gases, radioactivity or temperature (Wang and Xie, 2003). Different minerals and gases within the geothermal waters have proven to have different curative abilities. The use of carbolic water is thought to have significant medical importance for circulatory and heart disorders (Skapare *et al*., 2003). Sulphated water may heal hepatic insufficiency and problems with the accumulation of organic waste (Skapare *et al*., 2003). Bicarbonated water may relieve gastro-intestinal illness, hepatic insufficiency and gout (Skapare *et al*., 2003). Sodium chlorinated water may cure chronic infection of the mucous membrane (Lund, 2000; Skapare *et al*., 2003).

Ancient Greeks and Roman prescribed drinking and bathing in geothermal springs for its therapeutic effects especially for ailments such as jaundice and rheumatism (Hoole, 2001; Spicer and Nepgen, 2005). Chinese people used the Huang hot spring on the Shahe River for treatment of various ailments (La Moreaux and Tanner, 2001; Spicer and Nepgen, 2005). The Ethiopians used geothermal springs for the treatment of various diseases, such as skin diseases, leprosy and other contagious diseases (Pankurst, 1990). The ancient Egyptians are believed to have used geothermal baths for therapeutic purposes since 2000 BC. Many of these springs became known as sacred sites, and later evolved as healing centres (Spicer and Nepgen, 2005).

2.4.3 Agricultural benefits

Thermal springs have been used for irrigation purposes from time immemorial. Chinese people have used geothermal springs since the time of the Jin Dynasty (AD 265-420) (La Moreaux and Tanner, 2001). During this period, the Cunzhou City geothermal spring in the Hunan province was used to irrigate rice paddies so that they could grow rice even during the winter season (La Moreaux and Tanner, 2001).

European Commission (1999) reported that 25% of the direct heat produced by geothermal springs is used for agricultural purposes, which can be subdivided into the following activities:

- Agricultural crop drying
- Aquaculture
- Mushroom farming
- Heating greenhouses and irrigation

The agricultural uses of the geothermal spring depend on the surface temperature of the spring which have been summarized in Table 2.1 below.

Table 2.1: Temperatures required for various agricultural activities

Temperature in °C	Agricultural uses
20 – 25	Soil heating
35 – 95	Heating greenhouses
35 – 95	Food processing
20 – 40	Aquaculture
35 – 50	Biogas processing
45 – 65	Mushroom cultivation
65 – 95	Drying fruits and vegetables
50 – 70	Pasteurisation
60 – 85	Beet sugar extraction
70 – 100	Blanching and cooking
110 – 125	Sugar pulp drying

Source: **Popovski and Vasilevska, 2003**

Geothermal resources can be classified as low temperature (less than 90°C), moderate temperature (90°C -150°C) and high temperature (greater than 150°C). South African geothermal springs can thus be classified as low temperature geothermal resources and can be used for activities that require temperatures below 70°C (European Commission (EC), 1999; Geo-Heat Centre, 2005) (as indicated in Table 2.1). There is real potential for some of these geothermal resources to be used to dry locally produced fruits and vegetables, mushrooms and flowers. Siloam and Tshipise springs are located in rural areas and utilising these resources would benefit the rural communities and improve the socio-economic status of the rural population.

2.4.4 Tourism and recreation benefits

Tourism is currently responsible for the development of many geothermal springs into spas or resorts, and many spas are changing their focus to recapture the essence of a true spa's contribution to health and well-being. Currently about 15 million Europeans immerse themselves daily in geothermal spring waters (Hoole, 2001; Spicer and Nepgen, 2005). Forty-eight countries were using geothermal springs as resorts in the year 2000 (Lund and Freeston, 2001). This does not include data on countries such as South Africa, Malaysia, Ethiopia, Mozambique and Zambia since these countries did not submit data to the Geothermal World Conference of 2000, although it is a known fact they do have geothermal springs and spas for recreational use (Lund and Freeston, 2001).

Tshibalo (2011), reported that 31 out of known South African geothermal springs are used for recreation and tourism purposes. Recreational and tourism facilities and activities in South African geothermal spring resorts include the following facilities and activities: exercise areas, rest areas, restaurants, ladies' bars, shops, solariums, camping facilities, conference facilities, cocktail lounges, picnic sites, golf courses, tennis and squash courts, volleyball, snooker and pool, bowls, heated and cold swimming pools, hot mineral pools, jacuzzis, paddle boats, caravan and camping, game drives, birdwatching, and horse riding (Tshibalo, 2011).

2.5 Geothermal springs in South Africa

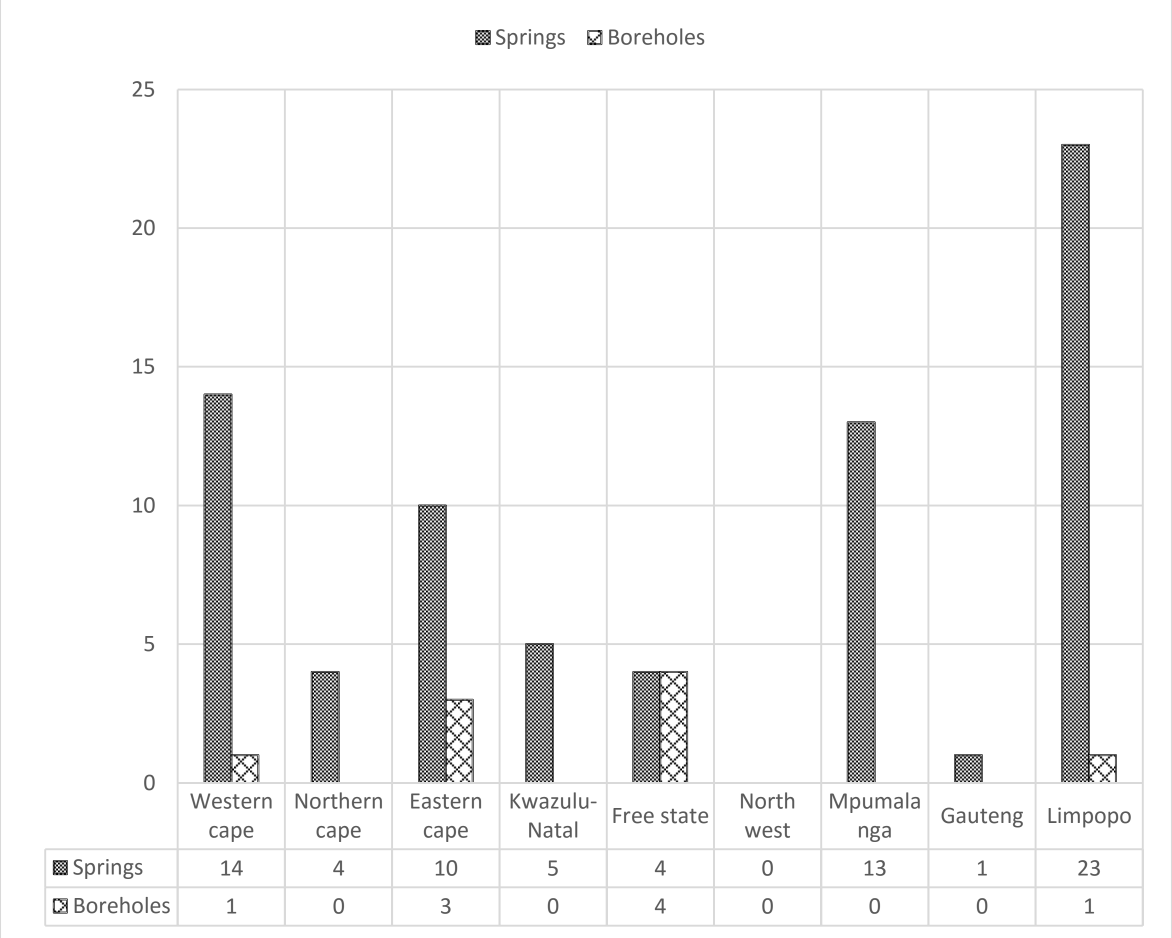
South African geothermal springs are considered to be associated with rainfall, faulting and shearing (Olivier *et al*., 2010). They are usually situated in topographically low areas with the surrounding elevated terrain serving as the catchment area for rainfall that permeates downwards through fracture planes in rocks into narrow conduits. The narrow conduits allow water to percolate to a deeper level where it is heated. The impermeable parts of faults, fracture zones or dykes restrict water percolation and cause water to rise to the earth's surface (Kent, 1969).

South Africa has about seventy-four known geothermal springs. Limpopo Province has more geothermal springs than any of the other provinces, with twenty-three geothermal springs with associated boreholes (Hoole, 2001; Olivier *et al.*, 2011). Olivier *et al*. (2011) reported that the geothermal sources at Sulphur springs, Tugela, and Windhoek are geothermal boreholes and not naturally-occurring springs while Vetfontein, Paddysland, Stindal, and Makutsi geothermal springs could not be located.

The mineral content of these geothermal springs are influenced by the type of rocks through which the water percolates (Kent, 1969). The South African geothermal springs extend into the distance past. The Khoi (Hottentots) used the geothermal spring at Caledon, calling it 'a fountain of life'. They believed that it could cure any type of illness and if the water was drunk, it made old men become 'active like the younger ones' (Boekstein, 1998). The geothermal spring at Montagu was also frequented by the Khoi and the San (Rindl, 1936).

Early western settlers in what became known as the Western Cape Province, started visiting the geothermal springs in this part of the world in the late 1600s and early 1700s, predominantly for health reasons. It was believed that bathing in the geothermal water cured ailments such as rheumatism (Booyens, 1981). Geothermal springs in Limpopo, namely Letaba (Die Eiland) and Bela Bela (Warmbaths) were also used before the arrival of the first Europeans. Letaba (Die Eiland) geothermal spring was used by indigenous people to produce salt by “lixiviating the mud through which the water issued and evaporating the resultant solution over the open fire in clay pots” (Kent, 1942). The spring was also used as a place where people would go and be cleansed as part of purification and spiritual harmonisation after battle (Ntsoane, 2001).

In South Africa, thermal waters were initially used for domestic and irrigation purposes, and later developed as health resorts and tourism destinations (Hoole, 2001). Figure 2.2 shows the number of geothermal springs with some associated boreholes per province in South Africa.



	Western cape	Northern cape	Eastern cape	Kwazulu-Natal	Free state	North west	Mpumalanga	Gauteng	Limpopo
▨ Springs	14	4	10	5	4	0	13	1	23
☒ Boreholes	1	0	3	0	4	0	0	0	1

Figure 2.2: Distribution of geothermal springs with associated boreholes per province (Olivier *et al*., 2008)

2.6 Geology of the Soutpansberg Group

The Soutpansberg Group overlies the eastern part of the Limpopo Mobile Belt, as well as the Palala Shear Zone and parts of the Kaapvaal Craton (Johnson *et al*., 2006). This Belt formed between two major crustal blocks, namely, the Kaapvaal Craton in the south and the Limpopo Mobile Belt in the north (Brandl, 1986). Deposition started with basaltic lava. This was followed by sedimentary rocks. Then, there was an erosional period, in which a pink massive quartzite covering a much larger area than the original rift was deposited.

Until the deposition of the Karoo rocks the Soutpansberg rocks formed a flat featureless landscape. Only after sedimentation had ceased (about 150 million years ago) was the area strongly block-faulted and then uniformly tilted to the north (Johnson *et al*., 2006). The landscape seen today is formed from the erosion during the last ± 60 million years (Cheney *et al*., 1990). The pink resistant quartzite was instrumental in shaping the present morphology. The Soutpansberg rocks which developed in a half-graben subsided along a main border fault situated most probably some 10–20 km south of the present Soutpansberg mountainous area (van Eeden *et al*., 1955).

Rocks of the Soutpansberg Group occupy a wedge-shaped, mountainous area, which stretches from Kruger National Park in the east, where it is at its widest, up to the Blouberg in the west, where they wedge out against a Fault on the northern side (Johnson *et al*., 2006). The strike of rock beds is east-west and the dip is moderate to steep to the north. The group is classified into seven formations and they are affected by a number of faults of various geological ages. These faults have probably had a considerable influence on the processes of sedimentation as well as the associated igneous activity. The trough in which the Soutpansberg Group has been deposited represents an ancient fault trough with a long life span, similar to an aulacogen (Jansen, 1975).

Eruptive activity within the basin was centred mainly on Sibasa, with smaller centres near Nzhelele Dam and the Blouberg (Johnson *et al*., 2006). However, the absence of marine sediments in this trough, as would be expected in the aulacogen, and the feeding of sediments into this trough from the north, and not parallel to its length, as would be required for an aulocogen, testifies against what was carried out by Jansen (1975). Thus, the Soutpansberg trough is viewed as a yoked intracratonic to the Limpopo Mobile Belt or near-cratonic environment (Johnson *et al*., 2006).

Table 2.2 summarises the lithostratigraphy of Siloam and Tshipise geothermal springs areas.

Table 2.2: Lithostratigraphy of Siloam and Tshipise geothermal springs areas

Sampling site	**Surface geology**	**Lithostratigraphic Unit**
Siloam	Basalt, minor tuff	Sibasa Formation, Soutpansberg Group
Tshipise	Basalt, minor andesite	Letaba Formation, Lebombo Group, Karoo Super Group
	Cream-coloured sandstone	Tshipise Member, Clarens Formation, Karoo Super Group
	Dolerite sills and dykes	Karoo dolerite, Stayt Formation

Source: **Kent (1949, 1969) and Olivier *et al*. (2011)**

2.6.1 Stratigraphy of the Soutpansberg Group

The Soutpansberg rocks rest unconformably on gneisses of the Limpopo Mobile Belt and Bandelierkop Complex. Along the eastern and most of the northern margin, the Soutpansberg outcrops are unconformably overlain by or tectonically juxtaposed against rocks of the Karoo SuperGroup (Johnson *et al*., 2006). The contact relationship between the Soutpansberg and Waterberg Group rocks is a tectonic one, though the latter rocks are believed to be younger (Johnson *et al*., 2006). The Soutpanberg Group is best developed in the eastern part, where the maximum preserved thickness is about 5000 m (Cheney *et al*., 1990). The Soutpansberg Group comprises a volcano-sedimentary succession which is subdivided into seven formations; Tshifefe, Sibasa, Fundudzi, Wylie’s Poort, Nzhelele, Stayt and Mabiligwe (Brandl, 2002; Johnson *et al*., 2006). Stayt Formation for Tshipise and Sibasa Formation for Siloam have been discussed briefly.

Stayt Formation

In the South-west of Tshipise there is a predominantly volcanic series of rocks, with accompanying sedimentary succession. The series rests on the floor of rocks belonging to the Beit Bridge Complex but its roof is not well-established (Johnson *et al*., 2006). The rocks are nearly horizontally disposed and consist of basal conglomerate, followed by considerable thickness of lava. The latter is followed by reddish, brown and purple shale, with pale-coloured quartzite, in which pebble beds are intercalated at the top (Cheney *et al*., 1990). The thickness of the Formation varies between 1700 and 1800 m, and it is regarded as correlative of Sibasa Formation, on the strength of a radiometric age of 1769 ± 34 Ma (Barton, 1979).

Sibasa Formation

The Sibasa Formation is dominantly a volcanic succession with rare discontinuous intercalations of clastic sediments, having a maximum thickness of about 3000 m. The volcanic comprise basalts, which were sub-aerially extruded and minor pyroclastic rocks. The basalts are amygdaloidal, massive and generally epidotised. The clastic sediments which include quartzite, shale and minor conglomerate, can reach locally a maximum thickness of 400 m. A radiometric age of 1749 ± 104 Ma was obtained (Johnson *et al*., 2006).

2.7 Physical characteristics of the geothermal springs

2.7.1 Flow rates

Geothermal springs can be classified according to the rate at which they discharge water, which is called the flow rate (discharge) (La Moreaux and Tanner, 2001). The flow rates of geothermal springs range from tiny seeps to high-rising water that shoots upwards and the rate is determined by the size of the aquifer, the extent of recharge (rainfall), the aquifer storage capacity, and the transmissivity and discharge capacity of both the aquifer and the conduit through which water rises to the surface (La Moreaux and Tanner, 2001).

The discharge of a hot spring can also be influenced by weather patterns, especially in areas characterized by sinkholes and fractured rocks, where floods and rainwater are directed into the ground (Witcher, 2002; Helfrich *et al*., 2005). Most geothermal springs are located at topographically low points. The difference in altitude between the recharge area and the exit point determines the hydrological head, which directly affects the flow rate. The flow rate is an important measurement since it is used to estimate water storage and supply, changes in water availability and water use rates (Helfrich *et al*., 2005).

2.7.2 Temperature

Geothermal springs can also be categorised according to their temperature and a temperature of 25°C is generally used to distinguish geothermal from non-geothermal springs. La Moreaux and Tanner (2001) reported that a spring with a temperature ‘significantly higher’ (that is, by 6°C) than the mean annual air temperature of the surrounding area, is regarded as geothermal. In view of the fact that the climate of one region differs from that of another, what is ‘warm’ in one region may not be considered to be such elsewhere. Therefore, the definition of a geothermal spring is often based on the mean annual air temperature of the specific site. However, the lack of a specific ‘base’ temperature may cause difficulties in interregional comparisons (La Moreaux and Tanner, 2001).

In some countries a defining temperature of around 20°C is used, following the climatological usage of this temperature to separate ‘mild’ from ‘warm’ climates (Kent, 1949). It is generally accepted that the boundary between ‘warm’ and ‘hot’ is that of the normal human body temperature (37°C) (Olivier *et al*., 2008). The classification of springs may also be influenced by the use of the spring, for instance, Table 2.3 shows the classification used by balneologists. Table 2.3 reveals that the Siloam and Tshipise springs are examples of scalding springs (Olivier *et al*., 2011).

Table 2.3: Balneological temperature classification

Category (Class)	Temperature
Cold spring	Below 25ºC
Tepid spring	Between 25ºC – 34ºC
Warm spring	Between 34ºC – 42ºC
Thermal spring	Between 42ºC – 50ºC
Scalding spring	Above 50ºC

Source: **Kent, 1949; Taylor and Phillips, (2007)**

Brandvlei in Western Cape Province is usually considered to be the hottest spring in South Africa (64°C), however Siloam (Limpopo) was found to have had a temperature of 67.5°C in 2004 (Olivier *et al.,* 2011). Although both the flow rate and the temperature of Siloam spring water have decreased over the last 5 years coming down to 63.5°C (Yibas *et al.*, 2011), the most recent field data recorded a temperature of 70°C (Yibas *et al.*, 2011). Other scalding geothermal springs are: Tshipise in Limpopo Province (57°C), Tugela Valley in KwaZulu Natal Province (52 – 53°C), Warmbaths in Limpopo Province (52°C), Olifants Valley in Western Cape Province (50 – 51°C), and Badplaas in Mpumalanga Province (50°C) (Yibas *et al.*, 2011).

Temperature can thus be used as a “tracer” of hydrogeological processes (Hartnady & Jones 2007). The temperature of groundwater provides insight into the subsurface geological processes that generate and transport heat (Witcher, 2002). The temperature of thermal springs is influenced by the temperature of the magma (for volcanic springs), the depth of penetration, as well as the nature of conduits of water to the surface (Kent, 1949). Although the faster the water comes to the surface, the less chance it has to cool down and thus the hotter it is (Kent, 1949; Hoole, 2001; Witcher, 2002).

2.7.3 pH

Geothermal springs that are characterised by low pH levels (acidic) are unlikely to be utilised as this adversely affects the survival of living organisms around them. As a result of this, acidic springs are unlikely to be used for domestic, recreational and agricultural purposes (New Mexico Environment Department, 2002).

Low pHs of the springs might be attributed to dissolution of carbonic rocks from weathering processes of the parent rocks, which the springs flow through (Zhou *et al*., 2006). Metals tend to dissolve more in low water pH and this could have health implication when deleterious heavy metals like lead and cadmium are washed into the spring via runoff (Zhou *et al*., 2006). Low values of alkalinity, which ought to have served as a buffer to the spring against sudden changes in pH might also be responsible for generally low pH, especially during acid precipitation. Currently most resorts or spas operate at thermal springs that are alkaline. The water suitable for swimming and bathing normally ranges between 6.5 and 8.3 in terms of its pH level because water below this level is likely to cause eye irritation (Hoole, 2001).

Some geothermal springs in the same geographic region show different water characteristics. The various springs probably originate from different depths and thus reflect variations in the geological structure within the area. Low water pH could lead to corrosion (Nordberg *et al*., 1985).

2.7.4 Electrical Conductivity and Total Dissolved Solids

Electrical conductivity (EC) is a measure of the capacity of water to conduct electrical current, and is directly related to the concentration of salts dissolved in water, and therefore to the total dissolved solids (TDS). Salts dissolve into either positively charged or negatively charged ions, which conduct electricity (Hayashi, 2008). The World Health Organization (2003) describes TDS as “the inorganic salts and small amounts of organic matter present in solution”. The principal constituents are usually calcium, magnesium, sodium, potassium (cations) and carbonate, hydrogen carbonate, chloride, sulphate and nitrate (anions). If the electrical conductivity of water is high this indicates a high concentration of ions which then determines if water is drinkable or not (Bruvold and Ongerth, 1969). The relationship between the EC and TDS is given below (eqn. 6);

$$A\ (\text{mg/L}) = 0.67 * B\ (\mu\text{S/cm}) \quad \text{……..…………….………………………eqn. 6}$$

Where A – TDS, B – EC, (Hayashi, 2008)

The electrical conductivity of water depends on the water temperature: the higher the temperature, the higher the electrical conductivity would be (Cassidy *et al*., 2001). The electrical conductivity of water increases by 2-3% for an increase of 1 degree Celsius of water temperature. Electrical conductivity is an indicator of total dissolved substances (TDS) and is based on the presence of ions (Hayashi, 2008). In a geothermal spring, high temperature implies high electrical conductivity values, which are indications of dissolved minerals in water (Olivier *et al.,* 2011). Most South African thermal springs have TDS concentrations in the region of 250-4000 mg/L and thus belong to classes A and B, which can be classified as slightly or highly mineralized waters as seen in Table 2.4 below (Bond, 1946). A commonly used classification system for thermal springs is that devised by Bond in 1946. He divided thermal spring waters into five categories as shown in Table 2.4 below;

Table 2.4: Classification of thermal spring water in South Africa

Class	Water	Chemical Composition
A	Highly mineralised chloride-sulphate waters	*TDS > 1 000 mg/L; Cl^- > 270 g/Kg; $SO_4 \geq 50$ g/kg
B	Slightly saline chloride waters	TDS 300 – 500 mg/L; Cl^- > 270 g/Kg; $SO_4 \leq 3$ g/Kg
C	Temporary hard carbonate waters	TDS < 800 mg/L; pH > 7.6
D	Alkaline sodium carbonate waters	TDS < 1 000 mg/L; Na_2CO_3 or $NaHCO_3$ > 150 mg/L No permanent hardness
E	“Pure” waters	TDS < 150 mg/L; pH < 7.1
*TDS-total dissolved solids		

Source: **Bond, 1946**

2.8 Chemical characteristics of geothermal springs

2.8.1 Elemental composition

The mineralogical composition encompasses both cations and anions present in water, which include sodium, potassium, calcium, magnesium, fluoride, chloride, carbonate, phosphate and nitrate/nitrite concentrations in water.

***Sodium* (*Na*)**

Sodium is a cation in common salt found in groundwater which can impart a salty taste at concentrations of over 250 mg/L (Gray, 2008). It can contribute to hypertension and high levels of sodium in drinking water should be noted by users on low sodium diets. A slight taste may be apparent above 100 mg/L (Johnson and Scherer, 2009). The concentrations of sodium in Siloam and Tshipise springs were 66.24 and 143 mg/L, respectively (Olivier *et al*., 2010).

***Potassium* (*K*)**

Potassium is a cation in common salt found in groundwater, which is essential in human diet. Excessive amounts in drinking water may have a laxative effect on humans. Acceptable concentration in drinking water can range from 0 to 8 mg/L (Johnson and Scherer, 2009). Previous study by Olivier *et al*. (2010), shows that the concentrations of potassium in Siloam and Tshipise springs were 2.82 and 4.25 mg/L, respectively.

***Calcium* (*Ca*) *and magnesium* (*Mg*)**

Calcium is a naturally occurring metal essential for human diet and is common in groundwater. Calcium concentration alone is not of major concern but with magnesium, they are the main contributors to the hardness of water (Gray, 2008). Maximum limits have not been established for calcium. However, magnesium concentrations above 125 mg/L may cause diarrhoea in some people (Johnson and Scherer, 2009). Previous work on Siloam and Tshipise springs show that the concentrations of calcium are 1.40 and 5.58 mg/L and the concentrations of magnesium are 1.30 and 0.17 mg/L, respectively (Olivier *et al*., 2010).

***Chloride* (*Cl^-*)**

Chloride is commonly found in groundwater. High concentrations of chloride ions can cause water to have a salty taste, corrode hot water plumbing systems and have a laxative effect on some people (Gray, 2008). A concentration below 200 mg/L has no undesirable health effects because World Health Organisation (2003) and European Union (1998) recommend 250 mg/L. The chloride concentrations at Siloam and Tshipise geothermal springs are 44.35 and 168.97 mg/L respectively, which are suitable for drinking without further treatment (Johnson & Scherer, 2009; Olivier *et al*., 2010).

***Fluoride* (F^-)**

Fluoride is a non-metal which occurs naturally in groundwater. It promotes dental health at concentrations of between 0.7 and 1.5 mg/L (Gray, 2008). At concentrations above 1.5 mg/L, dental fluorosis (a brownish staining of the teeth) may occur (SABS, 1999; WHO, 2000). Previous studies show fluoride concentrations at Siloam and Tshipise springs were 6.11 and 5.63 mg/L, respectively, which are above the South African guidelines for drinking water (Olivier *et al*., 2008; 2010). Since the concentrations do not fall within the recommended range for drinking water, geothermal water at Siloam and Tshipise are not suitable for drinking with regards to this mineral element.

***Sulphate* (SO_4^{2-})**

Sulphate is a constituent of a common salt found in groundwater, which can impart a salty taste. Drinking water with high quantities of sulphate can result in diarrhoea (Gray, 2008). With a concentration less than or equal to 200 mg/L sulphate, no adverse health effects are anticipated (Johnson and Scherer, 2009). The concentrations of sulphate in Siloam and Tshipise springs were 9.26 and 53.17 mg/L, respectively (Olivier *et al*., 2010), contributing to no adverse health effect.

***Nitrate* (NO_3^-)**

Nitrate is a very soluble anion and is dissolved by rainwater and percolates deeper into the soil where it enters groundwater by direct percolation. This makes nitrate the commonest chemical contaminant of groundwater (Spalding and Exner, 1993). WHO (2000) has set a standard of nitrate in drinking water as 10 mg/L; thus, Siloam and Tshipise spring waters are within the standard, having 0.00 and 0.61 mg/L, respectively (Olivier *et al*., 2010). The inclusion in the primary regulations is to protect against methaemoglobinaemia in infants under the age of 6 months (Gray, 2008).

2.8.2 Trace elements in geothermal springs

There are many trace elements in geothermal spring water, and these include: Li, Be, B, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Sn, Sb, Cs, Ba, La, W, Hg, Tl, Pb, Bi and U.

Antimony (*Sb*)

Antimony is a silvery white earth metal which can be toxic at high concentrations. It occurs naturally in the environment. Exposure to antimony at high concentrations in drinking water can result in increase in blood cholesterol and a decrease in blood sugar (Gray, 2008).The guideline value for antimony is 20 µg/L (WHO, 2008), while stricter limits have been set by the European Community and South African Guidelines as 5 µg/L and U.S Environmental Protection Agency with maximum contamination level (MCL) of 6 µg/L.

Arsenic (*As*)

Arsenic (As) is a semi-metallic element that occurs in a wide variety of minerals, mainly as As_2O_3, and can be recovered from processing of ores containing mostly copper, lead, zinc, silver and gold. It is also present in ashes from coal combustion. Arsenic exhibits fairly complex chemistry and can be present in several oxidation states (-III, 0, III, V) (Smith *et al.*, 1995). A high concentration of arsenic in drinking water can cause cancer, nausea, vomiting, diarrhoea and decreased production of red and white blood cells, and damage to blood vessels. The guideline value for drinking water is 0.01 mg/L (WHO, 2008; SABS, 1999). Previous study by Olivier et al. (2010) shows that the concentration of arsenic in Siloam and Tshipise spring water were 0.27 µg/L and 0.14 µg/L, respectively.

Barium (*Ba*)

Barium is a metallic element belonging to the alkaline earths. It is present as a trace element in both igneous and sedimentary rocks. Its guideline value in drinking water is 0.7 mg/L (WHO, 2008). There is no evidence that barium is carcinogenic (causing cancer) or mutagenic (causing changes in genetic mutation). The greatest concern to humans is its potential to cause hypertension (WHO, 2008). At Siloam and Tshipise springs, the concentration of barium were 4.22 µg/L and 13.63 µg/L, respectively (Olivier *et al*., 2010).

Beryllium (*Be*)

Beryllium is not an organic metallic element which does not degrade nor can it be degraded. It occurs naturally in drinking water. The primary concern with beryllium exposure is the lung disease caused by inhaling beryllium, and intestinal lesions. According to the United States Environmental Protection Agency (EPA), MCL of beryllium is 4 µg/L (New Hampshire Department of Environmental Services, 2007). Be was undetected in the study carried out by Olivier *et al*., 2010)

Boron **(*B*)**

Boron is a soft, brown crystalline non-metallic element extracted chiefly from kernite and borax. It is found naturally in groundwater and its provisional guideline value by WHO (2008) is 0.5 mg/L. EPA recommends concentrations below 0.6 mg/L for lifetime exposure to boron in drinking water (Usuda *et al.*, 2007). Boron concentration at Siloam and Tshipise were found to be 57.91 µg/L and 200.60 µg/L, respectively (Olivier *et al*., 2010).

Cadmium **(*Cd*)**

Cadmium is a rare natural element which is widely distributed in the earth's crust in very small amounts (Water UK, 2001). It is a soft, bluish-white metal. Its guideline value is 0.005 mg/L (EU, 1998) and 0.003 mg/L (WHO, 2008). When people breathe in cadmium, it can severely damage the lungs and may even cause death. Utilisation of cadmium by animals via eating or drinking could sometimes lead to high blood-pressure, liver disease and nerve or brain damage (Gray, 2008). A maximum acceptable concentration of 0.005 mg/L (5 µg/L) for cadmium in drinking water has been established on the basis of health considerations (Jarup *et al*., 1998). Previous study by Olivier *et al*. (2010) shows the concentrations of cadmium at Siloam and Tshipise are 0 µg/L and 0.02 µg/L, respectively.

Chromium **(*Cr*)**

Chromium is a metal found in natural deposits as ores containing other elements. Chromate and dichromate also adsorb on soil surfaces, especially iron and aluminum oxides. Cr (III) is the dominant form of chromium at low pH (<4). Cr^{3+} forms solution complexes with ammonia, hydroxide, chloride, fluoride, cyanide, sulphate and soluble organic ligands. Cr (VI) is the more toxic form of chromium and is also more mobile. Cr (III) mobility is decreased by adsorption to clays and oxide minerals below pH 5 and low solubility above pH 5 due to the formation of $Cr(OH)_3(s)$ (Chrotowski *et al*., 1991). Chromium mobility depends on sorption characteristics of the soil, including clay content, iron oxide content and the amount of organic matter present. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and un-adsorbed chromium complexes can leach from soil into groundwater. The leachability of Cr (VI) increases as soil pH increases and most chromium released into natural waters is particle associated (Smith *et al*., 1995). The guideline value for drinking water are 0.05 mg/L (WHO, 2008) and 0.1 mg/L (SABS, 1999). Chromium has the potential to cause the following health effects from long-term exposure at levels above MCL set by EPA: damage to the liver, kidney, circulatory system, nerve tissues and skin irritation. A study by Olivier *et al*. (2010) found the concentrations of chromium in Siloam and Tshipise spring water as 0.97 and 0.70 µg/L, respectively.

***Cobalt* (*Co*)**

Cobalt is an element that occurs naturally in the environment in air, water, soil, rocks, plants and animals. Co is widely dispersed in the environment and humans may be exposed to it by breathing air, drinking water and eating food that contain cobalt (George, 2003). Body contact with soil or water that contains cobalt may also enhance exposure. Exposure to cobalt may cause weight loss, dermatitis, and respiratory hypersensitivity. International Agency for Research on Cancer (IARC) has listed cobalt and cobalt compounds within group 2B (agents which are possibly carcinogenic to humans). Previous study by Olivier *et al*. (2010) shows that the concentrations of cobalt in Siloam and Tshipise spring water were 0.05 µg/L and 0.01 µg/L, respectively.

***Copper* (*Cu*)**

Copper is a reddish metal that occurs naturally in rocks, soil, water, sediment and air. Copper and its compounds are widely distributed in nature, and this element is found frequently in surface water and in some groundwaters (Alloway and Ayres, 1997). Copper is an essential and beneficial element in human metabolism and is generally considered non-toxic except at high doses (WHO, 2008) and the guideline value is 1 mg/L. The acute lethal dose for adults lies between 4 and 400 mg of copper (II) ion per kg of body weight, based on data from accidental ingestion and suicide cases (Agarwal *et al*., 1990). Individuals ingesting large doses of copper present with gastrointestinal bleeding, haematuria, intravascular haemolysis, methaemoglobinaemia, hepatocellular toxicity, acute renal failure and oliguria (Agarwal *et al*., 1990). At lower doses, copper ions can cause symptoms typical of food poisoning (headache, nausea, vomiting and diarrhoea). Previous study by Olivier *et al*. (2010) shows the concentrations of copper at both springs as 0 µg/L.

***Lanthanum* (*La*)**

Lanthanum is a white soft metallic element that tarnishes readily. It occurs in rare earth minerals and is classified as one of the most reactive rare earth mineral (Lenntech, 1998-2009). La is used to produce catalysers and to polish glass as well as zeolite catalysts used in petroleum refining owing to its stability at high temperature. It can be a threat to the liver when it accumulates in the human body. In marine animals, lanthanum can destroy the cell membrane, which may have negative consequences for reproduction and the functions of the nervous system. The Australian guideline value is 2 µg/L (NHMRC, 2004). Previous study by Olivier *el al*. (2010) reported 0.01 µg/L for Tshipise and was not determined at Siloam.

***Lead* (*Pb*)**

Lead is a metal found in natural deposits as ores containing other elements. It is generally used in household plumbing materials. Lead released to groundwater, surface water and land is usually in the form of elemental lead, lead oxides and hydroxides, and lead metal oxyanion complexes (Smith *et al*., 1995). Most lead that is released to the environment is retained in the soil. The primary processes influencing the fate of lead in soil include adsorption, ion exchange, precipitation, and complexation with absorbed organic matter. These processes limit the amount of lead that can be transported into the surface water or groundwater. The relatively volatile organo-lead compound tetra-methyl lead may form in anaerobic sediments as a result of alkylation by microorganisms (Smith *et al*., 1995). The amount of dissolved lead in surface water and groundwater depends on pH and the concentration of dissolved salts and the types of mineral surfaces present. The U.S Environmental Protection Agency (EPA) has set the MCL of water at 0 mg/L because it believes the level of protection would not cause health problems (USEPA, 2009). Exposure at levels above the MCL has the potential to cause strokes, kidney disease and cancer. The South Africa drinking water guideline value is 0.02 mg/L (SABS, 1999) and 0.01 mg/L (WHO, 2008). A study by Olivier *et al*. (2010) shows the concentrations of lead in Siloam and Tshipise spring water as 0.05 µg/L and 0.08 µg/L, respectively.

***Lithium* (*Li*)**

Lithium is a soft, silvery white metal that becomes yellowish upon exposure to moist air (Salocks and Kaley, 2003). Lithium carbonate and lithium salts are used in medicine to treat bipolar disorder and as an antidepressant. Physical tolerance differs between individuals and ingestion of excess amounts of lithium is toxic. At 10 mg/L, one is mildly poisoned (Lenntech, 1998-2009). Its effects on humans include abdominal pain, nausea, vomiting and diarrhoea, loss of muscle coordination, muscle rigidity and exaggerated reflexes. Mineral waters contain 0.05-1 mg/L of lithium and 17.05 µg/L and 94.24 µg/L were determined in Siloam and Tshipise geothermal springs, respectively (Olivier *et al*., 2010).

***Manganese* (*Mn*)**

Manganese is a naturally occurring metal, important in the human diet. Mn is reactive when pure and as a powder it will burn in oxygen; it reacts with water (its rust like iron) and dissolves in dilute acids (Lenntech, 1998-2009). According to Johnson and Scherer (2009), a high concentration of manganese does not appear to cause a health hazard. However, manganese concentration greater than 0.05 ml/L can cause brown and black stains on laundry, plumbing fixtures and sinks. The guideline value for drinking water is 0.05 mg/L (Kempster *et al*., 1997) and 0.1 mg/L (SABS, 1999). A study by Olivier *et al*. (2010) shows the concentration of manganese in Siloam and Tshipise spring water as 0.75 µg/L and 0 µg/L, respectively.

***Mercury* (*Hg*)**

Mercury is a liquid metal found in natural deposits as ores containing other elements (APEC, 2010). Mercury is a toxic element, with particularly damaging effects on the brain and central nervous system. It serves no beneficial physiological function in man. The main toxicological effects of mercury include neurological damage, paralysis, blindness, and chromosome breakage (Alloway and Ayres, 1997). Mercury concentration above the guideline value can cause kidney damage in humans and animals. The maximum acceptable concentration for mercury is set at 1 µg/L (WHO, 2008) which was adopted by the EC in drinking water directive, while the USEPA MCL has been set at 2 µg/L. Surface water and groundwater are generally well below this level. A study by Olivier *et al*. (2010) found mercury concentrations at Siloam and Tshipise as 0.53 µg/L and 0.33 µg/L, respectively.

***Molybdenum* (*Mo*)**

Molybdenum is a silvery white metal which can be attacked slowly by acids. It is a valuable alloying agent but toxicity does occur at >100 ng/kg of body weight resulting in diarrhoea, anaemia and elevated uric acid in the blood (Gray, 2008). It is an essential element in plant nutrition. Some plants can have up to 500 ppm of the metal when they grow in alkaline soil and the recommended daily intake for the mineral is 75 µg as a food supplement (Lenntech, 1998-2009). Doses larger than 200 µg may cause kidney problems and copper deficiencies. WHO (2008) guideline value is 70 µg/L, while the National Health and Medical Research Council (NHMRC) (2004) of Australia set the guideline value at 0.05 mg/L. Molybdenum concentrations were 2.23 µg/L and 1.41 µg/L at Siloam and Tshipise, respectively (Olivier *et al*., 2010).

***Nickel* (*Ni*)**

Nickel is a silvery white, hard, malleable and ductile metal. It occurs in very low levels in the environment especially in drinking water (<10%) (Gray, 2008). It is generally used as an ingredient in the steel and other metal products. It may be found in slate, sandstone, clay minerals and basalt. It is a dietary requirement for many organisms. Nickel concentrations in plants are 1 µg/g (Gray, 2008) and concentrations of nickel higher than 50 µg/g can be toxic (EU, 1998). The human body contains about 10 mg of nickel (Gray, 2008). The guideline value for drinking water is 0.02 mg/L (WHO, 2003) and 0.15 mg/L (SABS, 1999). A study by Olivier *et al*. (2010) shows that nickel concentration in Siloam and Tshipise spring water is 0 µg/L and 37.19 µg/L, respectively.

***Platinum* (*Pt*)**

Platinum is a lustrous, silver-white, malleable and ductile metal. It is resistant to corrosion and tarnishing. Platinum has many uses which include making fine jewellery; its alloys are used in surgical tools, laboratory utensils, and electrical resistance wires. Platinum bonds are applied in medicine to cure cancer. Platinum compounds are used in tumour therapy (Alt *et al*., 1997). Platinum salts can cause several negative health effects such as hearing damage, DNA alterations, and can cause cancer and damage to organs such as the intestines and the kidneys, and to bone marrow (Lenntech, 1998-2009). According to WHO (2008), there is no guideline value that is recommended for platinum concentrations in water. Previous research reveals concentration of platinum as 0.01 µg/L at Tshipise and was not determined at Siloam (Olivier *et al*., 2010).

***Selenium* (*Se*)**

Selenium is a non-metallic chemical element found in natural deposits as ores containing other elements (Smith *et al*., 1995). The major use of selenium is as an alloying additive in the metallurgical industry to improve the properties of copper, lead and steel. The toxic effects of long-term selenium exposure in humans are manifested in nails, hair and liver. In drinking water, a health-based guideline value for drinking water of 0.01 mg/L is given (WHO, 2003) and 0.02 mg/L (SABS, 1999). The use of selenium's antioxidant and curative properties as a dietary supplement has shown a positive effect on the following health problems: AIDS, arthritis, asthma, cancer, cardiovascular diseases, reproduction, thyroid and viral infections (George, 2003). A study by Olivier *et al*. (2010) shows that selenium concentrations in Siloam and Tshipise spring water are 0.72 µg/L and 2.35 µg/L, respectively.

***Tin* (*Sn*)**

Elementary tin does not dissolve in water under normal conditions (T = 20^{o}C and pressure = 1 bar). The naturally occurring amount of tin (cassiterite) in soils and water is relatively small (George, 2003). Tin is possibly a dietary requirement for a number of organisms. This may be caused by its presence in gastrine, a stomach and intestinal hormone. Upon oral intake tin compounds may be toxic. It is unknown exactly how much tin contributes to toxicity. Inorganic tin compounds are generally non-toxic. Toxicity of other tin compounds varies strongly. Organic tin compounds are toxic to bacteria and fungi, whereas these are non-toxic to animals and humans. Naturally occurring tin compound rarely affect human health. Some tin compounds do cause adverse health effects. For example, TBT oxide causes skin irritations, breathing problems, vomiting, headaches and facial disorder (Lenntech, 1998-2009).

***Strontium* (*Sr*)**

Stable strontium is a naturally occurring trace element in the diet and body (Skoryna, 1981). It is a soft silver-yellow, alkaline earth metal (Lenntech, 1998-2009). It is a widely distributed element in the geosphere, natural water and human tissues. Its compounds are used to colour television picture tubes and to produce the colour red in fireworks (Usuda *et al*., 2007). There is no evidence of strontium toxicity, but there are reports from a strontium-rich area in Turkey that when ingested in excessive amounts, strontium caused rickets. Clinical observations in Turkey noted a marked reduction in bone pain for patients suffering from osteoporosis (a medical condition in which the bones become brittle from loss of tissue) and a significant clinical improvement in patients with postmenopausal osteoporosis (Usuda *et al*., 2007). The United States EPA has recommended that the level of strontium in drinking water should not exceed 4 mg/L. Previous research reveals concentration of strontium as 20.35 µg/L and 213 µg/L at Siloam and Tshipise, respectively (Olivier *et al*., 2010).

***Tellurium* (*Te*)**

Tellurium is a semi metallic, lustrous, crystalline, brittle, silver-white element (Lenntech, 1998-2009). It has the properties of both metals and non-metals and used as an additive to steel and is alloyed to aluminium, copper, lead or tin. Ingestion even in small amounts can cause dreadful halitosis and body odour. It is not harmful to the natural environment. Currently, there is no guideline value for drinking water. A study by Olivier *et al*. (2010) shows that tellurium concentrations in Siloam and Tshipise spring waters are 0.02 µg/L and 0 µg/L, respectively.

***Zinc* (*Zn*)**

Zinc is a trace element that is essential for human health and is one of the most mobile heavy metals in surface waters and groundwater because it is present as soluble compounds at neutral and acidic pH values (Gray, 2008). When people absorb too little zinc they can experience loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Zinc shortages can even cause birth defects. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis (Smith *et al*., 1995). The maximum allowable concentration and the permissible concentration of zinc in drinking water are 10 and 5 mg/L respectively, according to ISI. A study by Olivier *et al*. (2010) shows that zinc concentrations at Siloam and Tshipise are 3.46 µg/L and 2.48 µg/L, respectively compared to the WHO standard of 3000 µg/L (WHO, 2003).

2.9 Trace elements in the soil

In nature, trace elements accumulate in the soil during the weathering of geologic parent materials, and they tend to be immobile (Davies, 1992). The concentrations in soils are related to the overlying parent material based on the immobile nature of trace elements (Malini *et al*., 1995). Trace elements in soils are generally insoluble and exhibit strong adsorption. The effects of soil characteristics on trace element concentrations in soils have been studied by many soil scientists and some of the studies have been reviewed by Adriano (1986). Trace element sorption depends on pH and whether the element occurs in anionic or cationic form (Dudka and Markert, 1992). Cation sorption increases with pH, showing a steep increase within a small pH range, which is known as the “adsorption edge” (Adriano, 1986).

A high cation exchange capacity (CEC) or anion exchange capacity (AEC) allows soil to hold more cations or anions, than soil with a low CEC or AEC. The exchange capacity of a soil is related to other soil properties, such as organic matter, clay, and oxide content. Soil organic matter retains elements both through its exchange capacity and through specific sorption, especially for elements such as Cu, Co, Mn and B (Mezhals, 1996). Soil high in clay has more surface area for elements to adsorb and a higher CEC than soil low in clay. Oxides of Fe and Mn have high affinity for trace elements, and either sorb or occlude the trace elements (Mezhals, 1996).

Redox potential of soil can change the solubility of an element. When soil undergoes reduction reaction, some elements such as Fe, Cd, Ni, and Pb can form insoluble sulphide precipitates. Elements such as Mn and Fe become more soluble under reducing conditions, in the absence of sulphides. All of these factors control the trace element retention of soil (Adriano, 1986). Since parent material is responsible for the lithogenic trace element content of soils, it may be helpful to correlate trace element concentration in soils to parent materials (Malini *et al*., 1995).

Soils are important receptacles for trace elements and they naturally contain trace levels of these elements. The presence of trace elements in soil is, however, not indicative of contamination but is primarily due to the geology of the parent material that forms the soil (Burk *et al.,* 2011). Geothermal springs are rich in trace elements owing to dissolution of the rock as a result of the high temperature. Therefore, assessment of trace element fate, bioavailability and transport in surface water and groundwater is required in order to predict potential contamination and impacts on soil and vegetation (Burk *et al*., 2011).

2.9.1 Physicochemical factors affecting the transfer of the trace elements in the soil

Soil pH

Soil pH is the main variable controlling the solubility, mobility and transport of trace elements, as it controls metal hydroxide, carbonate and phosphate solubilities. Soil pH also affects ion pair and complex formation, surface charge, and organic matter solubility (Appel and Ma, 2001; Huang *et al*., 2005). Trace elements solubility can be strongly affected by small changes in pH values. Metal solubility and their ion activity decrease with higher pH. The release of trace elements from freshwater sediments after gradual reduction of pH was Ca ≡ Mn > Fe > Ni > Zn > Cd > Al > Pb > Cu, and depends on the solid compound that held the trace elements (Buyks *et al*., 2002).

Soil pH controls the movement of trace elements from one soil horizon to another, since trace elements can be held in the lattice of secondary minerals (1:1 and 2:1 clay minerals), adsorbed on Fe and Mn oxides, and carbonates, or precipitated as carbonates. For instance, Maskall and Thornton (1998) found increases in the proportions of readily mobile forms of Pb and Zn as pH fell below 5. Cattlet *et al*. (2002) observed a decrease of Zn^{2+} activity in the soil solution as pH increased. They concluded that the organic matter adsorption and the formation of franklinite accounted for this trend.

Soil pH affects trace elements sorption. Boekhold *et al*. (1993) observed that Cd sorption doubled for each 0.5 increase in pH from 3.8 to 4.9. In sandy soils, a unit increase in pH produced a 2- to 10-fold increase in ion sorption (Harter and Naidu, 2001). The type and concentration of electrolyte and the substrate control pH change (Harter and Naidu, 2001). Whereas the retention and release vary minimally for various cationic elements, these processes manifest large differences for those trace elements that form anionic chemical species such as As, Cr, or Se. The concentration of arsenate in solution, that is, the predominant inorganic species of As, decreases at low pH because of its adsorption (Manning and Goldberg, 1996). Tyler and Olsson

(2001) observed an increase in the concentrations of As, Se, Mo, Cr, Sb and U in soil solutions with increasing pH.

Soil Organic Matter

Organic matter can play a dual role in trace elements solubilities. Particulate organic matter, by virtue of its high CEC, can effectively adsorb trace elements (Adriano, 2001). High-molecular-weight organic compounds can also bind and strip trace elements from the solution, because they can be insoluble and therefore semi-immobile (Schmitt *et al.,* 2002). It has been reported that humic acids can increase Cd retention on kaolinite four times (Taylor and Theng, 1995) and the formation of stable organometallic complexes can lead to relatively lower mobility of Cu, Pb, Ni, Zn, and Cd (Karapanagiotis *et al*., 1991). It has also been observed that insoluble organic molecules decreases the availability of some elements, such as Cu or Pb, by the formation of insoluble complexes (Bataillard *et al*., 2003).

In contrast, Temminghoff *et al*. (1998) found that humic acids enhanced Cu mobility, but the process was strongly affected by Ca concentration and the pH of the soil solution. In general, however, low-molecular-weight compounds, such as fulvic acids, can remain in the soil solution and thus increase the mobility of bound metals (Naidu and Harter, 1998). Some authors have found that naturally-occurring dissolved organic matters can increase the mobility of some elements, such as Cd (Lasat, 2002).

Organic matter may also limit the precipitation of chloropyromorphite ($Pb_5(PO4)_3Cl$), because dissolved organic matter inhibits crystal growth (Lang and Kaupenjohann, 2003). Also organic ligands could affect crystallization of secondary minerals; organic coatings around the crystal seeds may inhibit or retard crystallization (Ma, 1996). Preferential flow paths can adsorb certain trace elements due to higher organic matter content compared to soil matrix (Bundt *et al*., 2001). In contrast, the soluble organic matter may increase the amount of trace elements in the soil solution by the formation of soluble organo-metallic complexes (Naidu and Harter, 1998).

Clay minerals content and soil structure

Clay-rich soils generally have higher retention capacity than soils with little or no clay (Murray *et al*., 2004). Cation sorption on clay minerals varies depending on clay nature and cation properties. Vermiculite adsorbs twice as much Cs than illite and 20 times more than kaolinite in a single cation suspension (Tamura, 1972 and Murray *et al*., 2004). Pb and Cu adsorption was higher than Zn, Ni, and Cd adsorption on illite, beidellite, and montmorillonite (Murray *et al*., 2004). Desorption followed the trend Pb > Cd > Cu > Ni > Zn for beidellite and Pb > Cd ≡ Cu > Ni > Zn for illite and montmorillonite (Rybicka *et al*., 1995). Tiller *et al*. (1984) found a Pellustert (containing montmorillonite and kaolinite) adsorbed more Cd, Zn, and Ni than a Haplohumox or an Udalf (containing illite, kaolinite, chlorite, and quartz) at low pH value (4.5), whereas at high-pH values (>6.5) Cd and Ni adsorption capacity of Udalf was higher.

Selectivity of trace elements cation adsorption varies with clay minerals. Vermiculite is very effective for adsorbing Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+} and Ni, and the selectivity is greater than in montmorillonite, apparently due to more specific adsorption sites (Malla, 2002). However, selectivity changes with cations, as Brigatti *et al*. (2004) found that montmorillonite adsorbed greater amount of Hg than vermiculite. Tiller *et al.* (1984) identified three types of reactions, each having different affinities for cations:

- those associated with iron oxides, which appeared to be controlled by metal ion hydrolysis;
- those associated with organic colloids; and
- those associated with 2:1 clay minerals with lower sensitivity to pH.

2.10 Trace elements in vegetation

Trace elements also called “micronutrients” are those nutrients required in extremely small quantities (less than 100 ppm in plant dry weight). They are essential for the correct functioning of many plant, animal and human biological systems (Fuller, 2009). Some trace elements such as Cu, Fe, Mn, Zn, B and Mo are considered plant nutrients. Some of them, such as Ni and Co are considered essential to plant growth, since Ni is a component of the enzyme urease and Co is present in some enzymes, such as dehydratases, mutases, transpherases and phosphatases (Fuller, 2009).

Some essential trace elements play a vital role in many physiological processes in trace amounts; several of these ions are required for growth, metabolism and development (Shi and Sengupta, 1995; Singh and Yunus, 2000). High levels of these trace elements could lead to a range of cellular damage through inactivation of bio-molecules by blocking essential functional groups or through the displacement of essential metal ions (Adriano *et al*., 1978).

Plants growing on soils with high concentrations of trace elements more often than not contain these trace elements in their tissues (Leavitt *et al*., 1979). The absorption of elements occurs through the root system, through diffusion or cation exchange on the surface of clay minerals (Brooks, 1972). The elements are then translocated to the aerial parts of the plants such as the leaves, bark and shoots. Some plants can accumulate elements in huge quantities without any negative impact on their physiology. The plant's ability to translocate elements from the roots to the aerial parts depends on the depth of its root system. Plants in arid and semi-arid environments have deep-rooted systems because they depend on the saturation zone, below the water table for their moisture (Otieno *et al*., 2005).

Vegetation, which has deep penetrating root systems can absorb elements from throughout the soil horizons, groundwater, and even underlying bedrock (Raju & Raju, 1999). Arid to semi-arid climates commonly have sparse vegetation cover, however many of the species present may be phraetophytes (have deep penetrating roots in excess of 100 m) and as a result, require sampling much greater depths (Hoffmann, 1989, Cohen *et al*., 1989). Some of these elements extracted are essential and important for the survival of the plant. The non-essential elements (some of which are toxic to the plant) are stored in the more extreme parts of the plant such as the outer bark, twigs and tree tops. A number of these toxic elements are heavy metals which are of economic value and are moved to the parts of the plants that are easiest to sample (Dunn et al., 1996).

Some trace elements such as Cd, Cr, Hg, Pb, Ba, Sn, As and Se have no function in plant nutrition, elements (Pais and Jones, 1997). Plants absorb only minute amounts of Pb and then mostly in the roots. However, plants, especially leafy vegetables like lettuce, cabbage, and spinach, can absorb Cd in roots, leaves, and to some extent in their fruits (Cakmak *et al*., 2009). There are few cases of severe contamination with Cd that have resulted in harm. Once they are present in the soil, trace elements may be up-taken and accumulated in plants; this is the way trace elements enter the human food chain.

Table 2.5 shows some essential trace elements and their typical range in the soil content (mg/Kg). Soil pH, organic matter content, CEC and temperature can affect uptake of trace elements by plants (Pais and Jones, 1997). Boron is moderately mobile and moves out of the rooting depth of coarse textured, acidic soils and soils that have low organic matter content (Pais and Jones, 1997). The levels of plant available forms of trace elements are generally very low in relation to the total quantity present in soils (Singh and Yunus, 2000). Some of these elements are not available for most plants to take up. Soil reaction has the greatest influence on availability of trace elements that are taken up by plants (Singh and Yunus, 2000).

Element absorption occurs through the root system, by diffusion or cation exchange at the surface of clay minerals as well as transpiration (Brooks, 1972). The elements are then translocated to the aerial parts of the plants such as leaves, bark and shoots.

Table 2.5: Essential trace elements in vegetation

Trace element	Chemical symbols	Mass number (amu)	Common forms in soil	Typical range of soil content (mg/Kg)
Boron	B	9	BO_3^{3-}	0.9 - 1000
Chlorine	Cl	35.5	Cl^-	18 - 806
Cobalt	Co	60	Co^{2+}, Co^{3+}	0.3 - 200
Chromium	Cr	52	Cr^{3+},Cr^{6+}	0.9 - 1500
Copper	Cu	63.5	Cu^{2+}	2.5 - 60
Fluorine	F	19	F^-	6 - 7070
Iodine	I	127	I^-	<0.09 - 80
Iron	Fe	56	Fe^{2+},Fe^{3+}	0.01 - 21%
Manganese	Mn	55	Mn^{2+}	<1 - 18300
Molybdenum	Mo	96	Mo^{6+}	0.07 - 5
Nickel	Ni	59	$Ni^{2+,}$ Ni^{3+}	0.1 - 1523
Selenium	Se	79	Se^{5+},Se^{6+}	0.03 - 2
Zinc	Zn	65	Zn^{2+}	1.5 - 2000

Source: **Wild, 1988 and Alloway, 1995**

CHAPTER THREE

RESEARCH METHODOLOGY

3.1 Research design

This research was aimed at determining the trace elements concentrations in the geothermal springs of Siloam and Tshipise and their impacts on the soil and the vegetation. It is a quantitative study which show the variation of trace element concentrations among the geothermal spring water, soil and vegetation. The study investigated the trace elements availability in a non-geothermal source of water, soil and vegetation at Riverside residence (University of Venda) to serve as a control.

Numeric data were obtained from experimental analyses which were used for appropriate statistical analysis. Correlation analysis, factor analysis and two-way analysis of variance (ANOVA) were carried out on the obtained concentrations from the spring water, neighbouring soils and vegetation at both sites, in order to establish a valid conclusion on the findings.

3.2 Sampling

The sampling exercise was carried out thrice per season, specifically in winter and summer seasons to establish seasonal effect on the parameters at the study sites and control site (Yahaya *et al*., 2009). The sampling was carried out from May – July (winter season) and September – November (summer season), 2014. Table 3.1 summarises the number of samples of geothermal spring water, neighbouring soil and vegetation per season.

Table 3.1: Summary of samples and geographic coordinates of the sites

Study sites	Coordinates	Type of samples	No of samples per		
			trip	season	Total sample
Siloam	22° 36’ 05.48" S	Geothermal water	2	6	12
	30° 10’ 23.01" E	Surface soil (5 points)	5	15	30
		Mangifera indica (Leaf and bark)	2	6	12
Tshipise	22° 53’ 09.66" S	Geothermal water	2	6	12
	30° 12’ 40.36" E	Surface soil	5	15	30
		Acacia robusta (Leaf and bark)	2	6	12
Control site Riverside (UNIVEN)	22° 58’ 40.12” S	Non-geothermal water	1	3	6
	30° 27’ 04.25” E	Surface soil	1	3	6
		Mangifera indica (Leaf and bark)	2	6	12
		Acacia robusta (Leaf and bark)	2	6	12
Total samples			24	72	144

Quality assurance/Quality control (QA/QC) were incorporated into geothermal spring water, soil and vegetation sampling investigation in order to enhance sample integrity, increase the confidence of analytical data, and to prevent reporting wrong positive values caused by contamination. Field blank and splits were ensured for water sample; rinse blank and splits for soil samples and extract splits for the vegetation samples.

3.2.1. Geothermal spring water samples

Geothermal spring water samples were taken from Siloam and Tshipise springs. Representative samples were obtained through random sampling, in which water samples were obtained from every part of the spring, where possible with a plastic cup (Figures 3.1A and 3.1B) as recommended by Harvey (2000). The plastic containers were rinsed properly with the spring water to avoid cross contamination. All the water samples were collected in 2L plastic containers before transporting them to the laboratory for sample pre-treatment. The geothermal water samples were allowed to cool before pre-treatment and preservation in the laboratory. A control sample was taken from a non-geothermal source of water at the University of Venda (UNIVEN).

A – Water sampling at Siloam geothermal spring

B - Water sampling at Tshipise geothermal spring

C – Water sampling at Riverside, UNIVEN

Figure 3.1: Sampling of geothermal spring water and non-geothermal water

3.2.2 Soil samples

The simple random sampling procedure adopted by Pleysier (1995) was followed. Representative samples were obtained by random sampling, in which surface soil samples were taken from every part around the geothermal spring (Figures 3.2A and 3.2B) as recommended by Harvey (2000). Soil samples were taken at distances of 5 meter intervals to 20 meters away from the geothermal springs at Siloam and Tshipise, starting from the geothermal springs themselves. Thus, soil was sampled from 5 points in each study site; in a circular manner at Siloam and lateral manner at Tshipise due to mountain obstruction. Figure 3.3 shows the sampling points locations with their codes: SS1 – SS5 (Siloam) and ST1 – ST5 (Tshipise) representing the surface soil samples from 0 – 20 m away from the geothermal springs. Representative samples were taken from the top soil of depth 0-15 cm with hand shovel and was put inside a sampling bag, preferably polypropylene bag. A control sample was also collected from non-geothermal spring area. All the soil samples were collected in the polypropylene bag and transported to the laboratory before sample pre-treatment.

A – Sampling the soil at Siloam

B - Sampling the soil at Tshipise

C – Sampling the soil at Riverside, UNIVEN

Figure 3.2: Sampling soil at and in the neighbourhood of Siloam and Tshipise geothermal springs and Riverside, UNIVEN as control

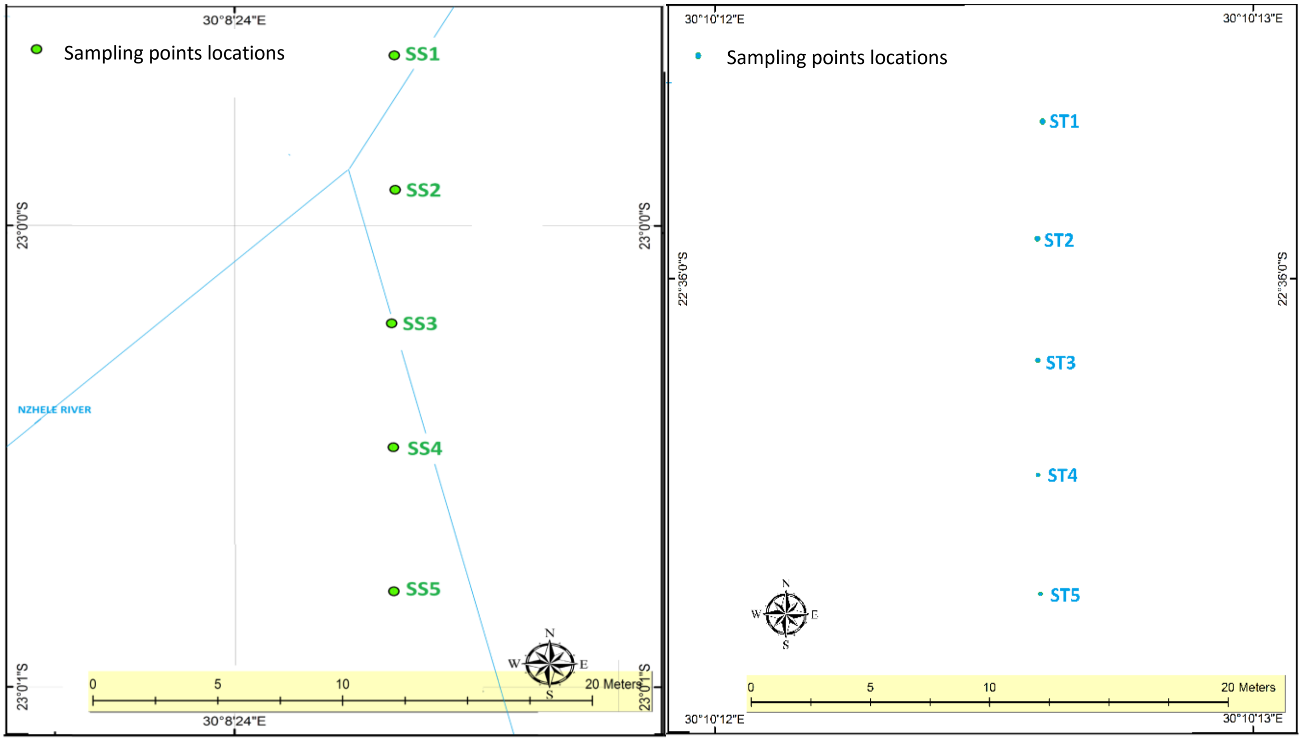


Figure 3.3: Locations of the sampling points of the soil at Siloam and Tshipise geothermal springs, respectively. SS1 – SS5 and ST1 – ST5 represent distance from 0 – 20 m away from the geothermal spring at Siloam and Tshipise, respectively.

3.2.3 Vegetation samples

The simple random sampling procedure was adopted for plant sampling (Pleysier, 1995). Vegetation samples were taken from the geothermal spring sites at Siloam, Tshipise (Figures 3.4A and 3.4B). The bark and leaf parts of the plant were sampled owing to their ability to accumulate trace elements from the soil (Pyle *et* al., 1996; Robinson *et al*., 2008). The vegetation samples were handpicked and a representative sample was obtained by taking a number of sample units randomly and combining them to form a bulk sample. The vegetation were within 10 m from the geothermal springs. All the vegetation samples were collected in the polypropylene bag and transported to the laboratory before the sample pretreatment. Botanists from Botanical Laboratory in the Department of Botany, University of Venda identified the plant to be *Mangifera indica* (Siloam) and *Acacia robusta* (Tshipise). *Mangifera indica* and *Acacia robusta* were chosen because they were plant species that grow around the geothermal springs at Siloam and Tshipise. The bark close to the soil and mature leaves of *Mangifera indica* and *Acacia robusta* were sampled owing to their ability to accumulate trace elements from the soil (Pyle *et al.*, 1996).

A – Sampling the leaves of *Mangifera indica* at Siloam

B – Sampling the bark of *Acacia robusta* at Tshipise

C – Sampling the leaves of *Acacia robusta* at Riverside, UNIVEN

Figure 3.4: Sampling of vegetation samples at Siloam, Tshipise and Riverside (control)

3.3 Experimental protocol

The experimental protocol of the research was subdivided into two segments based on seasonal variation. The first segment involved the winter sampling (May – July) and analyses involving the geothermal water, soil and the vegetation. The physicochemical parameters as well as trace element concentrations of the geothermal spring water and non-geothermal water were analysed and their impacts on the soil and vegetation were quantified. The second segment involved summer sampling (September – November) and analyses. The same studies for winter season were repeated for summer season to ascertain seasonal variation on the impacts of geothermal springs on the soil and vegetation.

All experiments were conducted under room temperature. The EC and TDS readings were expressed in mS/cm or µS/cm and mg/L, respectively, while the concentration of major cations and anions and trace elements were expressed in mg/L, µg/L and mg/Kg for water, soil and vegetation, respectively. The experimental analyses were conducted in triplicate to ensure quality assurance. Field measurements were carried out after proper calibration of the instrument (Figure 3.5).

Figure 3.5: Calibration for Multimeter (Multi 340i/SET) for field work

3.3.1 Chemicals

The reference materials used in this study were all standard chemicals from Agricultural research council-Institute for Soil, Climate and Water (ARC-ISCW), Pretoria South Africa. Certified purified traceable standard of 1000 mg/L of Ytterium and Indium (internal standards) for all the 28 trace elements with the major cations were used in the calibration of ICP-MS (Agilent 7700 series, USA) and ICP-OES (X-series 2, USA), respectively. Anions (F^-, Cl^-, NO_3, NO_2, SO_4, PO_4) standard combining NaCl, NaF, $NaNO_3$, $NaNO_2$, K_2SO_4 and KH_2PO_4 were used to calibrate Ion Chromagraphy (Dionex Model DX 500, USA). Metal salts used in the digestion processes include; HNO_3, HCl, $HClO_4$ and H_2O_2.

3.3.2 Sample pre-treatment

Water samples

The water samples were not filtered because there is need to analyse the water as it was being used, but acidified with concentrated HNO_3 to pH <2 (normally, 3 mL of conc. acid per litre of water samples) (USEPA, 2004). Preservation was carried out at the time of collection, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination. Acidification was carried out in the laboratory. The samples were mixed, held for 16 hours, and then verified to be pH <2 just prior to withdrawing an aliquot for processing or direct analysis were conducted. Water samples for major anions were kept at 4°C in the refrigerator and analysed within seven days of collection.

Soil samples

The pre-treatment of soil samples was carried out according to SR ISO 11466:1999. The soil samples were oven-dried by breaking down aggregates at 50°C for 8 hours. The dried soil samples were grounded (Figure 3.6 A) and sieved through 100 µm sieve. Then, the soil samples were labelled and kept in sealed plastic bags for analyses.

Vegetation samples

The pre-treatment of plant samples (bark and leaves) was carried out according to SR ISO 11466:1999. In this study, leaves and bark of the trunk were sampled for analysis owing to their ability to accumulate trace elements from root system via transpiration. The bark and leaf samples were intensely rinsed with tap water and deionised water, to eliminate soil and dust from the barks and leaves. Then, the samples were oven dried at 50°C for 8 hours, grounded (Figure 3.6 A) and then sieved through the 100 µm sieve. The samples were labelled and kept in sealed plastic bags until analyses were conducted.

3.4 Experimental analysis

3.4.1 Digestion analysis

The water samples were not digested because they were acidified during the sample pre-treatment as recommended in USEPA (2004). Samples were further diluted depending on the analyses to be carried out. For ICP-OES analysis (Major cations), there was no further dilution while there was 10 times dilution for ICP-MS analysis (28 trace elements).

The soil samples were digested using a microwave digestion system (SR ISO 11466: 1999). Approximately 1.0 g of pre-treated samples were digested with 9 mL HNO_3 and 1 mL H_2O_2. The solutions were allowed overnight and placed in the microwave for 30 minutes. After cooling, it was diluted to 50 mL with distilled water.

The vegetation samples (bark and leaves) were digested using Hot Block Method (NIOSH, 2003). A total of 0.5 g ground bark and leaf samples were weighed and 14 mL of 16 M HNO_3 was added. The solution was allowed to stay overnight and was placed in the block digestion system at initial temperature of 80°C for 30 minutes and increased at intervals of 10°C up to 120°C. Three to four drops of H_2O_2 were added and shaken for a few minutes, then allowed to cool for 20 minutes. Then, it was made up to 100 mL with de-ionised water and filtered with 15 mm size filter paper (ICP-MS analysis).

A total of 0.5 g powdery form of tree barks and leaf samples (Figure 3.6 A) were weighed and 7 mL 16 M HNO_3 with 3 mL $HClO_4$ was added and shaked then allowed overnight in the fume cupboard (NIOSH, 2003). The solution was placed in the block digestion system at initial temperature of 80°C for 30 minutes and increased at intervals of 10°C up to 180°C (Figure 3.6 B). Three to four drops of H_2O_2 were added and shaken for a few minutes, then allowed to cool for 20 minutes. Then, the solution was made up to 100 mL with de-ionised water and filtered with 15 mm size filter paper (ICP-OES analysis).

A - Grinding of the oven dried soil and plant samples

B - Digestion using Hot Block Method (Barks and Leaves)

Figure 3.6: Images of some selected experimental analysis carried out at ARC-ISCW

3.4.2 Water extract analysis from vegetation samples

The standard procedure for water extract from tree barks and leaves by Garltey (2011) was followed: Approximately 0.5 g of the barks and leaves were weighed and 50 mL of distilled water was added. It was then placed in a shaker for 30 minutes and allowed to cool; later placed in the centrifuge for 10 minutes at 50 rpm and filtered off with 100 mm filter paper to collect the water extract for EC, TDS and major anions analyses.

3.4.3 Saturated soil paste analysis

The saturated soil paste analysis was carried out according to Garltey (2011). The weight of the empty dish was noted and approximately 250 g of dried, sieved soil sample was added. Distilled water was added to the soil in the dish while stirring with a spatula. After thorough mixing, the samples were allowed to stand for 2 hours and weighed again to check for saturation. The saturated paste was transferred to a Buchner funnel with a 9 cm filter paper. A vacuum was applied and the saturated paste extract was collected in 250 mL vacuum flask. The extracts was analysed for EC, TDS and major anion.

3.4.4 Temperature, pH, EC and TDS analysis

The measurement of the pH, temperature, EC and TDS of the water samples were carried out *in situ* using Multimeter (Multi 340i/SET, USA) and also at the laboratory. The water extracts obtained from the bark and leaf samples were used to analyse for the pH, EC and TDS following Garltey (2011) procedure. The electrode was rinsed and the pH adjusted with a standard pH solution concentration followed by HCl or NaOH; the electrode was rinsed with distilled water, the water extract from barks and leaves samples was analysed for pH and EC using Mantech tritrasip autotitrator (Figure 3.7 A)

The saturated paste extract were analysed for pH, EC and TDS as proposed by Garltey (2011). After calibration of the instrument, the saturated paste extract from the soil samples was anlaysed for pH, EC and TDS using Mantech tritrasip autotitrator (Figure 3.7 A).

From the EC value obtained from the procedure above, the TDS can be calculated by the formular in equation 6. All the samples were measured in triplicate and the mean values were estimated per season.

3.4.5 Soil organic matter analysis

Soil organic matter (SOM) content was estimated from an ignition method proposed by Magdoff *et al*. (1996). An empty porcelain was weighed (W_1) and a known mass of the soil sample (W_2) was added together (W_3). The soil porcelain was placed in muffle furnace at 440°C for 12 hours and reweighed to know the weight of Ash (W_4). Weight of porcelain + ash (W_4) was deducted from weight of porcelain + soil (W_3) resulting to weight of ash (W_0). Then, weight of ash (W_0) was divided by the weight of soil (W_2) multiplied by 100.

$$\frac{W_0}{W_2} \times 100 \text{...eqn. 7}$$

All the soil samples were analysed in triplicate and the mean values were estimated and documented.

3.4.6 Major anions analysis

Water samples were filtered with a 0.45 µm filter paper before taking a subsample for analyses. The EC value obtained was an indicator for indicating if further dilution was necessary. EC value above 500 µS/cm requires 5 times dilution and above 1000 µS/cm requires 10 times dilution. The subsamples were poured into the auto sampler vials and analysed using IC (Dionex Model DX 500) (Figure 3.7 B) (USEPA, 1993).

The water extract from plant (roots and leaves) samples and saturated paste extracts from soil were further filtered using a 0.45 µm membrane type filter and then analysed using IC (Dionex Model DX 500) (Figure 3.7 B) after the EC values were known (USEPA, 1993). The samples were measured in triplicate and the mean values were estimated

3.4.7 Trace elements analysis

The procedures for the determination of trace elements in the vegetation (barks and leaves) and soil samples were adopted from Pais and Jones (1997); they are as follows: digested samples from microwave (soil) and block digester (bark and leaves) were filtered with 0.45 µm filter paper before taking a subsample for analyses. The major cations were analysed using ICP-OES without further dilution after calibration with the internal standard of the equipment. Trace elements were analysed using ICP-MS (Figure 3.7 C) after the background check up of the equipment. The mass spectrometry for lowest, medium and highest mass numbers were obtained (Appendix 1). The samples were measured in triplicate and the mean values were estimated.

The geothermal water samples were analysed for major cations using ICP-OES without dilution and trace elements using ICP-MS with a dilution factor of 10. All the measurements were carried out in triplicate to obtain a mean value.

A - Mantech Titrasip Autotitrator used for determination of pH, EC and alkalinity

B – Ion chromatograpy (Dionex Model DX 500) used for the determination of the major anions

C – Inductive coupled plasma-mass spectrometer (ICP-MS) (Agilent 7700 series) used for the determination of the trace elements

Figure 3.7: Some equipments used for analyses at ARC-ISCW

3.5 Data analysis and interpretation

Statistical analyses were conducted using the Statistical Package for Social Science (IBM Version 22) and Microsoft Excel 2013 (Microsoft Corp., Santa Rosa, CA). The chemical elements' concentrations and physico-chemical parameters of water, soils and plants were subjected to descriptive statistics and presented in tables, line graphs and charts. Data obtained from the hydro-chemical parameters were subjected to Piper chart to identify the main chemical compositions of the spring water, surface soils and vegetation. Piper diagram is a tri-linear diagram on which the concentrations of the major ions are plotted as percentages, with each point representing a chemical component of the samples. The two base triangles reflect the sample anions and cations concentrations, respectively.

Factor analysis was performed on trace element concentrations from the soil through the extraction method (principal component analysis). The rotation of the principal components was executed through the Varimax method with Kaiser Normalisation (Liu *et al*., 2003). Factor loading is the measure of the degree of closeness between the variables and a factor. The Rotation mode factor analysis provides several positive features that allow the interpretation of data sets.

The parameters analysed from geothermal spring water, soil and vegetation were subjected to ANOVA (Two factors without replication) to establish if there are significant differences ($P < 0.05$) in the samples in different seasons.

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Preamble

This chapter presents and discusses the results for all the experimental work conducted. These results relate to: concentrations of the trace elements from the geothermal springs, surface soils and vegetation around the geothermal springs. The impacts of these trace elements were quantified in the soil at different distances away (5 m interval) and in the vegetation. The results presented in this chapter are summarised mean values obtained from the analyses per season.

4.2 Physical and chemical characteristics of the geothermal springs

4.2.1 Thermal characteristics of the geothermal springs

The thermal property of the geothermal springs show slight variation with time (Figure 4.1). Previous work by Kent (1949) and Olivier *et al*. (2008; 2010) also reported slight changes in the thermal property of these springs which could not be accounted for. Figure 4.1 shows clearly the variations in the thermal property of the geothermal springs. Siloam recorded 67.5°C in 2004, 62°C in 2010, 67.7°C in winter season (2014), 68.6°C in summer season (2014) while Tshipise recorded 57.2°C in 1949, 58°C in 2004/2010, 54.6°C in winter season (2014), 55.7°C in summer season (2014). These changes can be attributed to seasonal variation which leads to the fluctuation of the thermal property of the springs. During the summer season, there is high rainfall and more underground water (coupled with high flow rate), which is heated as a result of the geothermal gradient of 2°C - 3°C per 100 m (Press and Siever, 1986). This results in high temperature in summer compared to winter season. At both sites, there is approximately 1°C difference in the thermal property of the geothermal spring in summer season compared to winter season. This high temperature in summer results in more transfer of moisture to the atmosphere until the dew point is reached, hence there is potential to rain more intensely this period.

The temperature obtained in the geothermal spring's water was higher compared to the control, which shows that there is a significant difference in their temperature. High water temperature in the geothermal spring aids in the more mineralisation of the water compared to the control sample (Odiyo and Makungo, 2012). The differences in the temperature in control sample could be attributed to the surrounding temperature since it is a borehole (Figure 4.1). Thermal properties of these geothermal springs have shown slight variations over ten years and more (Figure 4.2). The R^2 – values were less than 0.5 (0.15 for Siloam from 2004 – 2014 and 0.46 for Tshipise from

1949 – 2014), which implies that there is a weak correlation between the temperature of the geothermal springs and time. In each study site, the temperature obtained during summer season was not significantly different from the temperature obtained during winter season except for the control (Figure 4.1). This shows that the geothermal gradient of the springs is the major controlling factor.

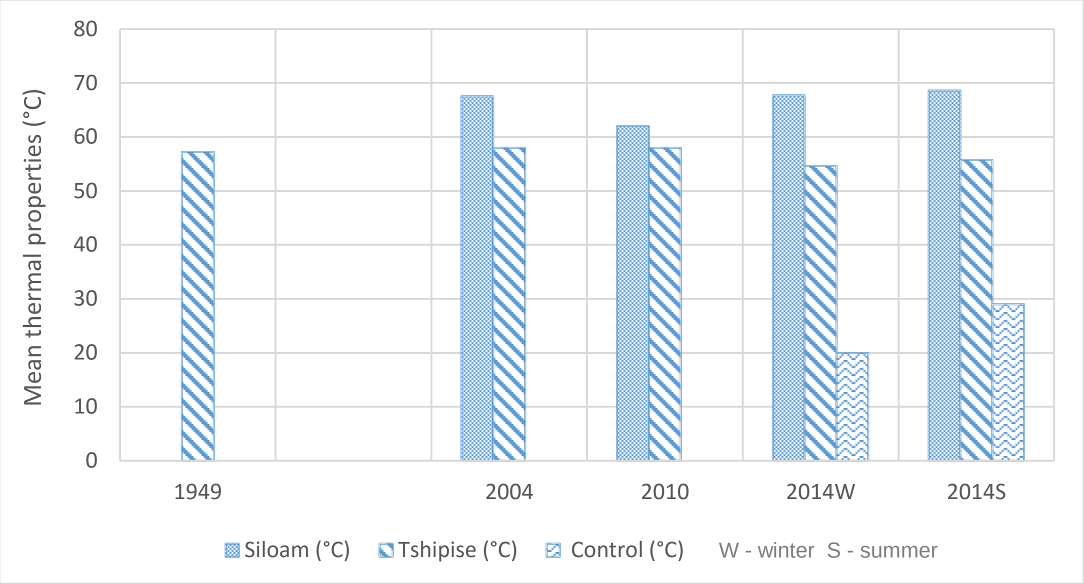
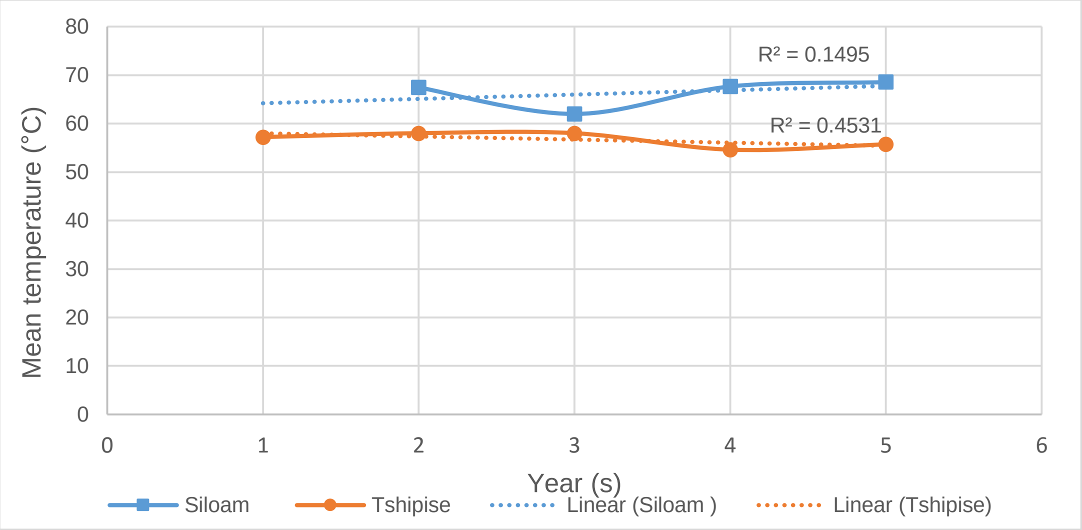


Figure 4.1: Comparison of the thermal properties from this study with previous studies (Kent, 1949 and Olivier *et al*., 2008; 2010)



Note: yr 1 – 1949, yr 2 – 2004, yr 3 – 2010, yr 4 – winter 2014 and yr 5 – summer 2014

Figure 4.2: Trend of temperature variation with studies by Kent and Olivier et al. 2008; 2010

4.2.2 Chemical composition of the geothermal springs

Geothermal springs are usually mineralized to a greater or lesser extent, depending on the geological formation associated with the circulating groundwater (Todd, 1980). Table 4.1 shows the results of the chemical composition of the geothermal spring water and a non-geothermal spring water (control). Results show that geothermal spring water is more mineralized than non-geothermal water and its mineralization could be due to the rock-water interaction at the deeper aquifer. Non-geothermal water falls within domestic water quality (DWAF, 1996) and WHO (2000) value for pH, SAR, EC and TDS. There is little or no differences in the chemical composition of the control sample at both seasons which could be as a result of the constant temperature of the water compared to the geothermal spring water.

The measured pH values are 9.43 and 9.57 at Siloam, 8.91 and 8.93 at Tshipise for winter and summer seasons, respectively. The control site pH is 7.71 for both seasons. The pH values obtained at Siloam exceeded the recommended South African Guidelines for Domestic Water Quality (DWAF, 1996) values of 7-9. The SAR values for Siloam and Tshipise were greater than one (>1). Therefore geothermal water is not suitable for irrigation. TDS values were 188.4 mg/L and 214 mg/L at Siloam; 428.4 mg/L and 467.49 mg/L at Tshipise for winter and summer, respectively. The TDS value at Tshipise in summer season (467.49 mg/L) exceeded the value for Domestic Water Quality (DWAF, 1996) value of 450 mg/L, although, the EC for Siloam and Tshipise were within the South African Guidelines.

A comparison of the present findings with previous studies in Siloam and Tshipise carried out by Olivier *et al*. (2008, 2010) (Table 4.1), reveals that the mineral composition of the geothermal water has remained partially constant over the last 6 years (2004 - 2010). The slight differences were probably due to the differences in fundamental changes in water chemistry, which result in seasonal variation in the compositions of the springs. The chemical composition of the studied geothermal water has shown slight variation in the two different season. The magnitudes of variations was not significant except for EC, TDS, Cl^-, SO^{2-}_4 and HCO_3^- having significant differences between summer and winter seasons at Siloam and Tshipise. These could be attributed to rainwater (Nelson, 2002) which causes more dissolution of cyclic salts; and connate salts in the Karoo strata of the Lebombo Group (Olivier *et al*., 2011) in the summer compared to winter season. Cl^- and SO_4^{2-} do not take part in typical biological or chemical reactions like other chemical constituents, they tend to concentrate in shallow groundwater over time (Nelson, 2002), hence they are high in both geothermal springs. The HCO_3^- concentration was higher in winter than in the summer season at both Siloam and Tshipise. This could be as a result of the less reaction between the HCO_3^- and cations particularly Ca^{2+} and Mg^{2+} in winter compared to summer, hence making the water alkaline.

Table 4.1 Hydro-chemical parameters of geothermal springs

	Control W	Control S	Literature data (s)		Tshipise W	Tshipise S	Siloam W	Siloam S
			Siloam	Tshipise				
Field analysis								
pH	7.70	7.72	nd	nd	8.51	8.68	8.77	8.87
Elect. conduct. (µS/cm)	nd	nd	nd	nd	1721.30	1731.00	707.30	695.70
TDS (mg/L)	nd	nd	nd	nd	1100.00	1110.00	453.00	445.00
Lab. analysis								
pH (6-9)	7.69	7.73	8.92;9.51	8.30;8.85	8.91	8.93	9.43	9.57
pHs (pHs-pH±1)	8.40	8.60	8.50;9.23	8.70;8.94	8.34	8.60	8.64	8.70
SAR (<1*)	0.46	0.46	2.83;14.82	15.93;25.43	**14.55**	**13.60**	**7.40**	**6.90**
Elect. conduct. (mS/m) (<150)	12.00	14.00	29.00;39.00	80.00;81.00	67.50	80.00	33.50	39.00
TDS (mg/L) (<450)	71.00	74.00	157.93;197.32	422.1;460.56	428.40	**467.49**	188.40	214.00
Alkalinity (mg/L)	58.00	60.00	nd	nd	157.00	111.50	106.00	104.50
Temp.Hard.(mg/L)	58.65	58.65	nd	nd	28.00	31.81	19.37	23.08
Cations (mg/L)								
Sodium (<200)	8.10	8.10	41.36;66.24	140.19;156.31	167.70	165.91	73.44	73.46
Potassium (<50)	1.42	1.44	2.42;2.82	3.51;4.25	4.20	4.18	2.65	2.56
Calcium (ns)	12.73	12.73	1.38;140	2.84;5.58	8.12	7.16	5.65	5.17
Magnesium (ns)	6.39	6.39	0.08;1.30	0.01;0.17	1.18	2.57	1.09	2.30
Anions (mg/L)								
Fluoride (1.5;1*)	0.11	0.11	**6.08;6.11**	**5.08;5.63**	**6.72**	**7.28**	**6.66**	**5.97**
Nitrate (<6*)	1.20	1.40	0.04;0.00	0.39;0.61	1.96	0.78	0.57	0.24
Chloride (<200)	4.93	4.93	43.44;44.35	158.60;168.97	97.04	161.17	24.65	48.01
Sulphate (< 400)	1.16	1.20	10.44;10.69	47.58;53.17	44.46	56.85	9.03	13.09
Phosphate (ns)	0.32	0.32	0.00;2.69	0.00;0.00	2.31	0.33	0.84	0.00
Carbonate (ns)	0.00	0.00	0.00;14.40	nd	7.05	5.70	15.75	16.50
Bicarbonate (ns)	71.96	72.00	nd	nd	177.21	111.02	97.30	93.94

ns = not stipulated, nd = not determined, W = winter, S = summer
Literature data were obtained from Olivier *et al*., 2008; 2010
Values in bracket: SABS (1999) and WHO (2000), *DWAF (1996)
Values in bold indicate exceedance of SABS (1999) and WHO (2000) guideline values

A Piper diagram (Figure 4.3) was used to illustrate the chemical composition of the geothermal waters as well as the water type. The explanation of the piper diagram is based on that of Piper (1944) as demonstrated in Sajil Kumar (2013). The water type for the non-geothermal water (control site) is Ca-HCO_3 at both seasons (Figure 4.3) which is dominated with Ca^{2+} and HCO^-_3 derived from the weathering of minerals in the bedrock, including calcite, the most easily weathered mineral in the aquifer. Ca-HCO_3 waters represent recharge waters with short residence times (Lipfert *et al*., 2004). Ca-HCO_3 water falls under temporary hard carbonate water (class C) according to Bond (1946) classification.

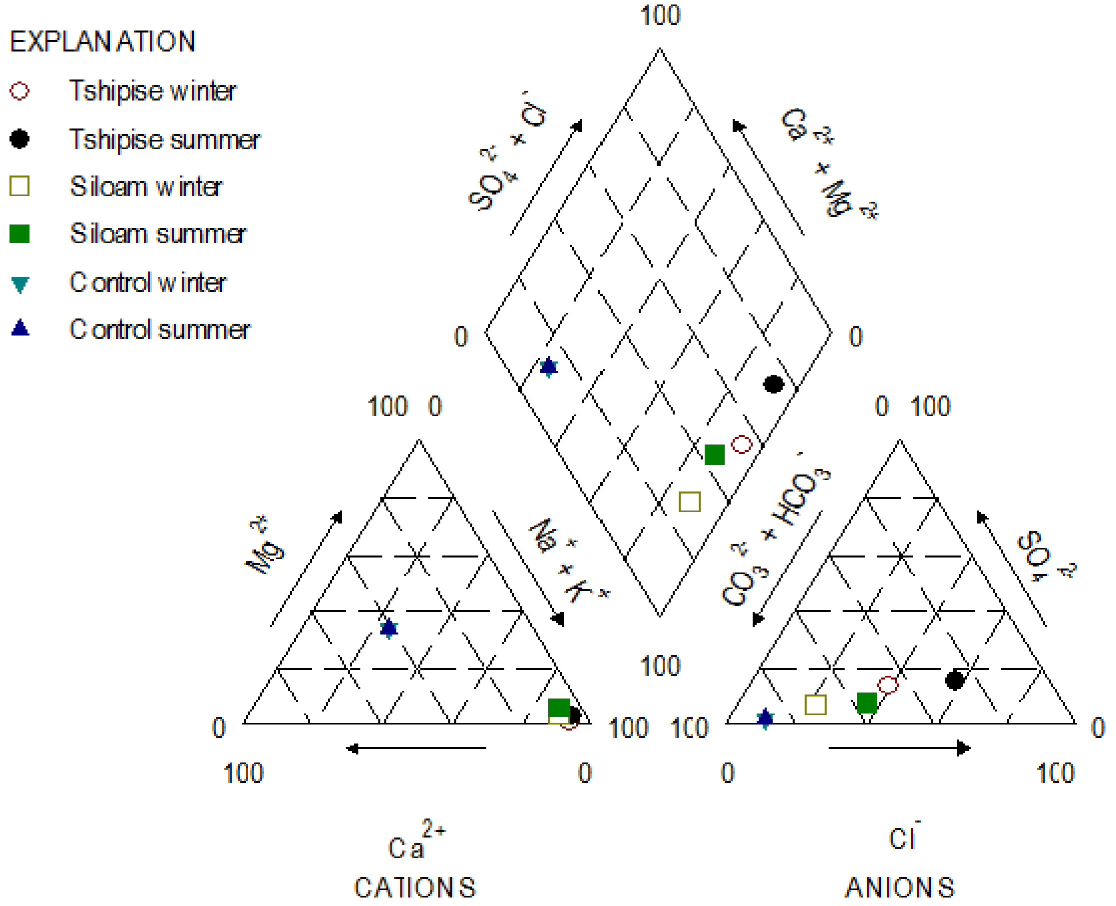


Figure 4.3: Piper diagram showing the chemical composition of the geothermal water and control sample

Figure 4.3 shows that the water type found in Siloam is Na-Cl which is dominated by Na^+ and Cl^-, derived from NaCl brines in winter and summer seasons. There is no variation in the water type with season. The Ca^{2+} and HCO^-_3 ions were also present, making the water type fall under class

C (temporary hard carbonate water) (Bond, 1946) as reported by Olivier *et al*. (2011). At Tshipise, Na-HCO_3 and Ca-NaHCO_3 represent the water type in winter and summer seasons, respectively. The Na-HCO_3 water type is the most evolved of the waters and derives their Na^+ from cation exchange of Ca^{2+} for Na^+ and K^+ as well as dissolution of rock mineral (plagioclase) (Lipfert *et al*., 2004). There was seasonal difference in the water type from Na-HCO_3 in winter to Ca-NaHCO_3 in summer season. This could be due to the rainfall in the summer season which aids in dissolution of rock mineral (plagioclase) and strong interaction between Na^+ and Ca^{2+} ion that leads to Ca-NaHCO_3. These findings support the previous studies by Oliver et al. (2011) as the water also falls under class C (temporary hard carbonate water) (Bond, 1946).

The chemical compositions of the geothermal springs have shown high F^- and SAR at both springs; high pH-value at Siloam and high TDS value at Tshipise. These factors have made the geothermal spring water unfit for drinking, particularly because of its high flouride content and pH values. In addition, it is not suitable for irrigation, owing to its high SAR value.

4.2.3 Trace elements concentrations in geothermal springs

Table 4.2 shows the mean values for trace elements concentrations in the geothermal springs and the non-geothermal spring, which implies that geothermal water are highly mineralized owing to the geological composition as supported by Todd (1980). The table also compares the present findings with the previous work carried out by Olivier *et al*. (2011) in 2010 as well as the standard guidelines for drinking water by SABS (1999) and WHO (2000).

According to the South African drinking water standards, the geothermal water contains unacceptably high values of Ni (868 µg/L; 462.11 µg/L) and Pb (652 µg/L; 211 µg/L) at Tshipise and Siloam, respectively, and high value of Hg in Tshipise during summer (Table 4.2). All the trace elements in the non-geothermal water fall within the SA and WHO water standards guidelines for drinking water, hence, making the non-geothermal water (control) suitable for usage. Trace elements concentrations in the control have remained practically the same or with little differences at both seasons. Comparison with previous study by Olivier et al. (2011) shows that there are differences in the concentrations of the trace elements, though the magnitude of the differences may not necessarily be much. This implies that there are reasonable differences in the trace elements concentrations of the springs over the last four years. These could be as a result of the anthropogenic factors. At each study site, there is a significant differences in the trace element concentrations in different seasons (ANOVA, $P < 0.1$) but no significant differences at

$P > 0.05$ ($0.05 < P < 0.1$). Siloam geothermal spring water was found to be more mineralised than Tshipise spring water and this could be as a result of the high water temperature in the spring.

Table 4.2: Mean trace elements concentrations in the geothermal springs and control in winter and summer seasons

Date		Literature data (2010)		2014					
	WHO; SABS	Siloam	Tshipise	Control W	Control S	Tshipise S	Tshipise W	Siloam S	Siloam W
Elements	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
Li		17.05	94.24	0.20	0.22	58.97	51.15	13.74	10.01
Be		0.00	0.00	0.04	0.04	0.05	0.04	0.04	0.04
B		57.91	200.60	1.01	1.01	31.23	18.27	4.83	0.03
Ti		6.14	3.03	0.53	0.53	1.23	2.25	3.27	3.99
V		2.30	1.81	0.96	1.00	0.15	0.03	3.20	2.63
Cr	50; 100	0.97	0.70	0.03	0.03	0.41	0.06	0.03	0.06
Mn	500; 100	0.75	0.00	1.72	1.74	7.20	0.63	1.34	0.19
Co		0.05	0.10	0.16	0.16	9.65	0.01	0.18	0.01
Ni	20; 150	0.00	37.19	2.62	2.64	**868.00**	0.05	**462.11**	0.63
Cu	2000; 1000	0.00	0.00	0.21	0.21	45.39	0.51	0.13	0.24
Zn	3000; 5000	3.46	2.48	50.70	58.70	348.00	0.17	342.00	0.12
As	10; 10	0.27	0.14	0.09	0.13	0.41	0.06	0.33	0.11
Se	10; 20	0.72	2.35	0.09	0.09	3.00	1.07	0.10	0.55
Rb		nd	nd	1.48	1.49	11.34	14.77	13.29	16.66
Sr		20.35	213.30	35.23	44.47	213.50	211.33	8.73	11.33
Mo		2.23	1.41	0.02	0.20	1.58	1.14	1.64	1.10
Cd		0.00	0.02	0.06	0.10	23.19	0.20	0.24	0.02
Sn		nd	nd	0.37	0.37	2.09	0.09	2.23	0.09
Sb	5; 5	0.00	0.02	0.01	0.01	0.71	0.01	0.02	0.01
Te		0.02	0.00	0.01	0.05	0.13	0.03	0.00	0.09
Cs		nd	nd	0.03	0.05	13.69	1.26	0.47	0.54
Ba		4.22	13.63	30.61	41.33	18.78	17.05	6.68	9.15
La		nd	0.01	0.30	0.34	0.12	0.02	0.01	0.02
W		0.45	4.19	0.05	0.07	4.42	2.73	0.87	1.27
Pt		nd	0.01	0.01	0.03	0.10	0.01	0.02	0.01
Hg	1; 1	0.53	0.33	0.02	0.02	1.78	0.25	0.64	0.04
Tl		0.00	0.01	0.01	0.01	0.42	0.04	0.01	0.04
Pb	10; 20	0.05	0.08	0.09	0.13	**652.00**	0.05	**211.00**	0.01
Bi		0.00	0.00	0.01	0.01	0.10	0.01	0.03	0.01
U		0.00	0.00	0.01	0.01	0.05	0.01	0.01	0.01

Nd = not determined, W = winter, S = summer
Literature data was obtained from Olivier *et al*. (2011)
Figures in bold are above the recommended maximum value for human use (SABS (1999); WHO (2000)).

Figure 4.4 shows clearly that the trace element concentrations follow the same trend but vary in magnitude of concentrations. Also, there are more trace elements in summer compared to the winter season. This can be attributed to the rainfall in the summer. Rainfall aids in more dissociation of rock particles and the release of abundant trace elements. Elements like Li, Be, B, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sn, Sb, Te, Cs, Ba, La, W, Pt, Hg, Tl, Pb, Bi and U are higher in concentrations in the summer than in the winter season at least in one of the two springs. Nevertheless, elements like Ti and Rb are higher in winter compared to summer. This might be as a result of their reactivity with water.

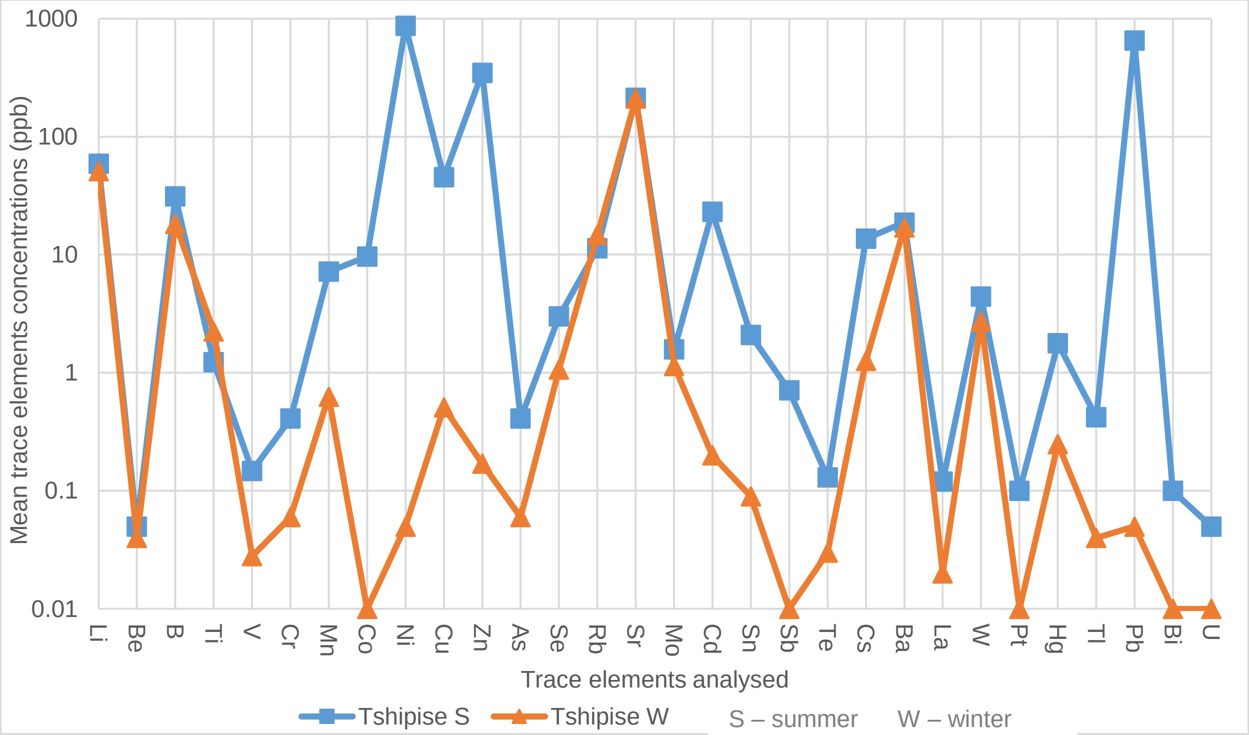


Figure 4.4: Seasonal variation of the trace elements concentrations in Tshipise Spring

At Siloam, there are significant variations in trace elements concentrations between winter and summer seasons (Figure 4.5). Also, there are more trace elements in summer than winter, similar to case of Tshipise spring. Elements like Li, B, V, Mn, Co, Ni, Zn, As, Mo, Cd, Sn, Sb, Pt, Hg, Pb and Bi, are higher in concentrations in summer compared to winter. However, Be, Ti, Cr, Cu, Se, Rb, Sr, Te, Cs, Ba, La, W and Tl are higher in concentrations in winter compared to summer while U remains constant in both seasons. Rb is denser than water and so sinks easily. Rb has a strong correlation with Be, Cs, Ba, La, Tl, Te, Cr, Cu, Se, Sr and Ti. This accounts for their higher concentrations in the winter compared to the summer season.

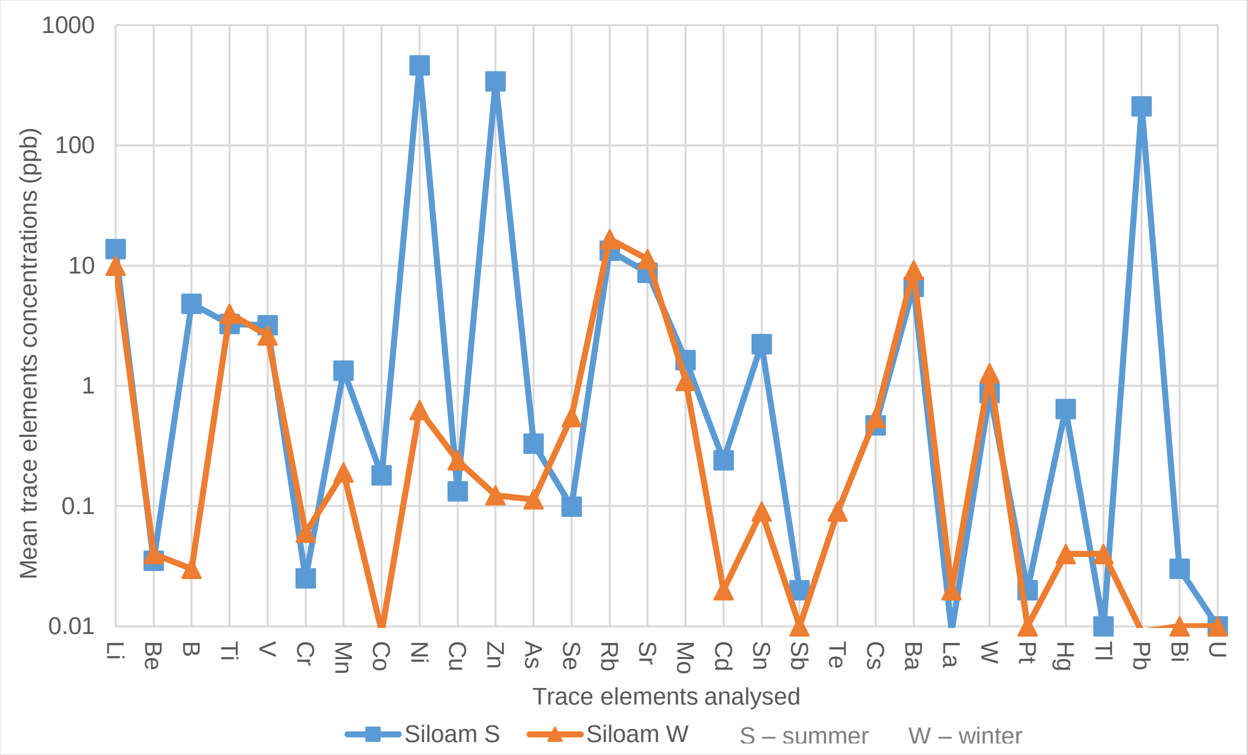


Figure 4.5: Seasonal variation of the trace elements concentrations in Siloam spring

4.2.4 Seasonal comparison of trace elements concentrations in the geothermal spring water

The mean trace elements concentrations in geothermal spring water in summer were mainly higher than in winter season (ANOVA $p < 0.1$, Tables 4.3A and 4.3B) for both Siloam and Tshipise springs. The statistical results imply that there were significant differences (P = 0.09) and (P = 0.08) for Siloam and Tshipise, respectively. Since the P-values were higher than 0.05, there is no significant differences at 95% level of confidence. However, at 90% level of confidence, there were significant differences in the trace elements concentrations between summer and winter seasons for both study sites.

The mean trace elements concentrations within the sites were in relatively good agreement during summer season and these account for seasonal variations in the concentrations of the trace elements in the geothermal water. As stated earlier, more rainfall in summer season enhances more rock- water interaction at the deep aquifer of the geothermal spring and more trace elements were released to the water body at the surface. Therefore, there are more trace elements in the geothermal water during summer than in the winter season.

Table 4.3: ANOVA for Siloam and Tshipise geothermal water

A - Siloam

Source of Variation	SS	df	MS	F	P-value	F critical
Between Groups	17277.72	1.00	17277.72	2.97	**0.09**	4.01
Within Groups	337395.50	58.00	5817.16			
Total	354673.21	59.00				

B - Tshipise

Source of Variation	SS	df	MS	F	P-value	F critical
Between Groups	66293.19	1.00	66293.19	3.15	**0.08**	4.01
Within Groups	1218716.62	58.00	21012.36			
Total	1285009.81	59.00				

4.3 Factor analysis on the trace element concentrations on the neighbouring soils of geothermal springs

Factor analysis carried out on the parameters analysed in water samples from both Siloam and Tshipise were subjected to factor analysis, and resulted in one factor. This only factor represents 100% of the total variance and is characterized by high loading of Li, Be, B, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Sn, Sb, Te, Cs, Ba, La, W, Pt, Hg, Tl, Pb, Bi, U, Na, K, Ca, Mg, F, NO_3, Cl, SO_4, PO_4, CO_3, HCO_3, pH, EC and Temperature. This factor is due to water-rock interaction resulting from the geothermal gradient at the deep aquifer. It also account for geochemical dissolution of rocks at high temperature of the water leading to more mineralisation, high pH (alkaline), electrical conductivity (EC) and total dissolved solids (TDS).

Factor analysis carried out on the concentrations of the trace elements in the surface soils from both Siloam and Tshipise suggests two factors in both winter and summer (Table 4.4). The first factor represents 91.78% of the total variance in winter season, with high loadings of Li, Be, Ti, V, Cr, Mn, Co, Ni, Cu, As, Se, Sr, Cs, La and Tl, and 76.37% of the total variance in summer with high loadings of Be, Ti, Cr, Mn, Co, Ni, Cu, Se, Sr, Ba, La, and Tl at Siloam soil. In Tshipise, the first factor represents 69.88% of the total variance in winter season with high loadings of Li, Be, B, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Sn, Ba, La and U, and 29% of total variance in summer season with high loading of Li, Be, B, V, Cr, Mn, Co, Ni, Cu, Se, Mo, Cd, Ba, La, Hg and Pb. This factor can be attributed to geothermal water-surface soil interaction in which the soil absorbs trace elements resulting to their accumulation. Geothermal water is used for irrigation purposes at both sites and there is high tendency of the trace elements mobility to the soil surface. Geothermal spring water flows across the soil surface, resulting in a high tendency of the trace elements from springs to be trapped in the soil.

Table 4.4: Factors derived from varimax R-mode factor analysis with Kaiser Normalisation of the trace elements concentrations of soils at Siloam and Tshipise

	Siloam				Tshipise			
	Winter		Summer		Winter		Summer	
Elements	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2
Li	**0.52**	**0.85**	0.30	0.22	**0.77**	0.46	**0.97**	-0.09
Be	**0.87**	0.49	**0.68**	0.09	**0.53**	0.45	**0.55**	0.12
B	0.47	-0.34	-0.12	-0.62	**0.81**	**0.55**	**0.67**	**0.74**
Ti	**0.82**	0.19	**0.99**	-0.04	**0.80**	**0.60**	0.43	**0.90**
V	**0.90**	-0.34	0.20	-0.75	**0.89**	0.34	**0.64**	**0.72**
Cr	**0.95**	-0.24	**0.51**	-0.76	**0.76**	**0.62**	**0.59**	**0.68**
Mn	**1.00**	-0.02	**0.97**	-0.23	**0.98**	0.20	**0.87**	0.34
Co	**1.00**	-0.06	**0.93**	-0.35	**0.90**	0.24	**0.81**	0.25
Ni	**0.97**	0.04	**0.96**	-0.13	**0.81**	0.44	**0.79**	0.48
Cu	**0.99**	-0.04	**0.83**	-0.49	**0.98**	0.19	**0.86**	0.42
Zn	-0.24	**0.97**	-0.07	**1.00**	**0.84**	-0.54	-0.70	**0.71**
As	**0.87**	0.02	-0.75	0.14	**0.88**	0.38	0.22	**0.91**
Se	**0.86**	-0.05	**0.70**	-0.56	**0.70**	0.44	**0.71**	**0.54**
Rb	0.48	**0.87**	-0.10	**0.80**	**0.81**	**0.50**	0.49	**0.77**
Sr	**0.95**	0.28	**0.74**	-0.12	**0.63**	0.38	0.35	-0.05
Mo	-0.55	**0.69**	-0.16	**0.75**	**0.85**	0.49	**0.61**	0.12
Cd	0.14	**0.94**	-0.36	**0.52**	**0.90**	-0.04	**0.76**	0.41
Sn	0.04	**0.98**	0.46	**0.57**	**0.87**	0.21	-0.04	-0.73
Sb	-0.74	0.33	-0.18	**0.84**	-0.81	-0.27	0.22	-0.74
Cs	**0.58**	**0.73**	0.44	0.34	0.08	0.39	0.15	**0.79**
Ba	0.34	**0.93**	**0.89**	0.25	**0.77**	**0.51**	**0.62**	0.23
La	**0.91**	0.40	**0.63**	0.10	**0.91**	0.28	**0.61**	**0.65**
W	-0.86	0.35	0.19	**0.71**	0.00	-0.30	-0.11	-0.58
Hg	0.37	-0.60	0.14	**0.84**	0.22	**0.93**	**0.80**	0.44
Tl	**0.98**	-0.04	**0.75**	-0.25	0.16	**0.63**	-0.05	0.49
Pb	-0.45	**0.85**	-0.24	**0.82**	0.33	0.34	**0.83**	-0.03
Bi	-0.31	**0.94**	-0.20	**0.80**	0.44	**0.65**	-0.17	0.02
U	0.12	-0.66	-0.42	-0.59	**0.99**	0.10	0.49	**0.84**
Total Variance	**91.78**	**7.03**	**76.37**	**22.12**	**69.88**	**26.99**	**29.00**	**70.48**

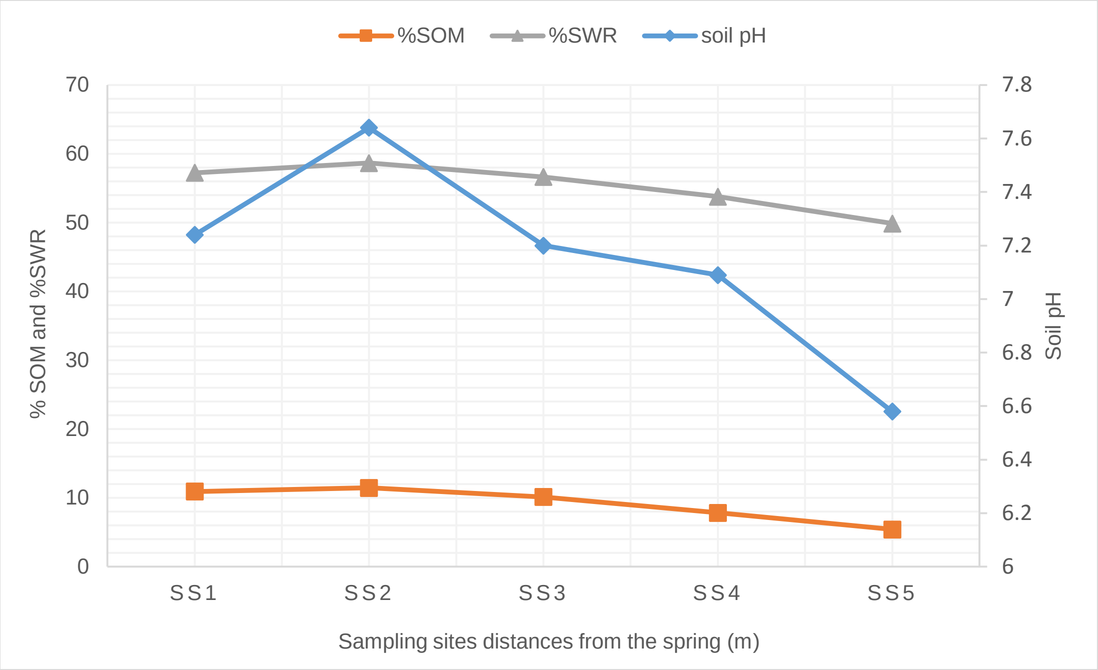
Note: In bold are high positive scores (≥0.50)

The second factor represents 7.03% of the total variance in winter with high loadings of Li, Zn, Rb, Mo, Cd, Sn, Cs, Ba, Pb and Bi, and 22.12% of the total variance in summer with high loadings of Zn, Rb, Mo, Cd, Sn, Sb, W, Hg, Pb and Bi at Siloam soil. In Tshipise, 26.99% of the total variance in winter with high loadings of B, Ti, Cr, Rb, Ba, Hg, Tl and Bi, and 70.48% of the total variance in summer with high loadings of B, Ti, V, Cr, Zn, As, Se, Rb, Cs, La and U. This factor is attributed to the soil pedogenesis and anthropogenic factors. Soil contains trace quantities of these elements based on its parent material and soil forming factors (soil pedogenesis) (Siegel, 2002). Table 4.4 reflects the seasonal variation in the availability of the trace elements in the soil, that is, the total variance of the first factor decreases from 91% to 76.37% ; 69.88% to 29% (winter to summer) in Siloam and Tshipise, respectively.

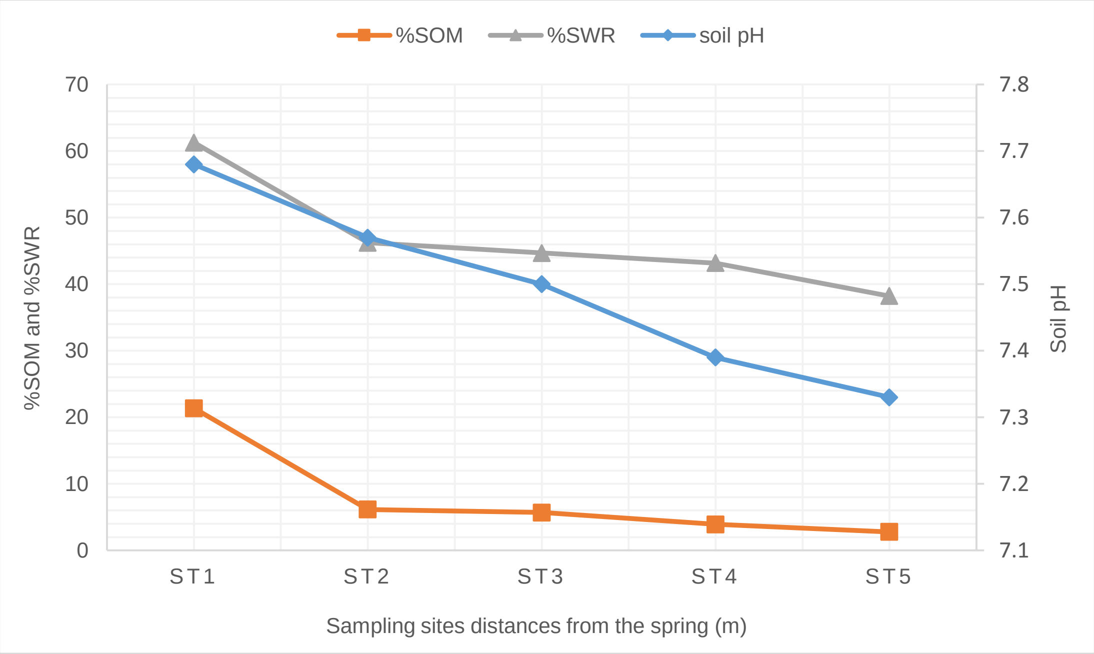
Total variance of the second factor increases from 7.03% to 22.12%; 26.99% to 70.48% (winter to summer) in Siloam and Tshipise, respectively. This variation can be attributed to rainfall in summer which promotes more reactivity and dissolution of parent rock (soil pedogenesis). During winter, geothermal water is solely used for irrigation in both sites and this accounts for high variance in the first factor while in summer, there is rainfall which serves as an alternative source of irrigation coupled with the geothermal water. This accounts for the increase in the total variance in the second factor for both sites.

4.3.1 Soil pH, soil organic matter and soil water retention as Indicators

Indicators such as soil pH, SOM and SWR (Figures 4.6A and 4.6B) could predict the availability of trace elements in the soil. SS1 - SS5 and ST1 - ST5 represent surface soil sampling points from 0-20 m away from geothermal spring at Siloam and Tshipise, respectively (Figure 3.3). This study shows that there is a good relationship between the indicators and trace elements in relation to the distance in such a way that the higher the soil pH, SOM and SWR of the soil, the higher the availability of these elements in the soil (Figures 4.6 and 4.7). Figures 4.6 A and B show clearly the decrease in indicator values with distance, which predicts the reduction in trace elements concentrations with distance. Studies of Ma *et al*. (1997); Burt *et al*. (2003); Chen *et al*. (1999) and Tack *et al*. (1997) show that there is little correlation between total trace elements and indicators. This study's findings are supported by studies by Adraino (2001) and Kabata-Pendias and Pendias (2001), which show that the trace elements attenuation capacity of soil increases with increasing pH, SOM and SWR. At 5 m away in Siloam (SS2), soil pH, SOM, SWR and trace elements concentrations are higher than at SS1 (distance closest to the source) (Figures 4.6A and 4.7). This can be attributed to the fact that the water from the geothermal spring continuously runs from the source to distances of 5 m away and up to 10 m, and therefore could be accumulating trace elements and affect the indicators in both seasons (Figures 4.6A and 4.7).



A – Siloam



B - Tshipise

Figure 4.6: Effects of the indicators on the soil at Siloam and Tshipise

The washing of the slaughtered chicken and plucking of their feathers by the members of the community in the neighbourhood of the geothermal spring (Figure 4.8) also contribute to increased SOM and hence contribute to the availability of the trace elements. At Tshipise, reduction of the indicators with distance (figure 4.6B) would also account for the decrease in the trace elements concentrations in both seasons (Figure 4.7). The indicators play a relevant role in the seasonality of the trace element concentrations; there are more trace elements at the summer compared to winter season (Figure 4.7). This shows clearly that is trace element availability is directly proportional to the presence of the indicator (pH, SOM and SWR).

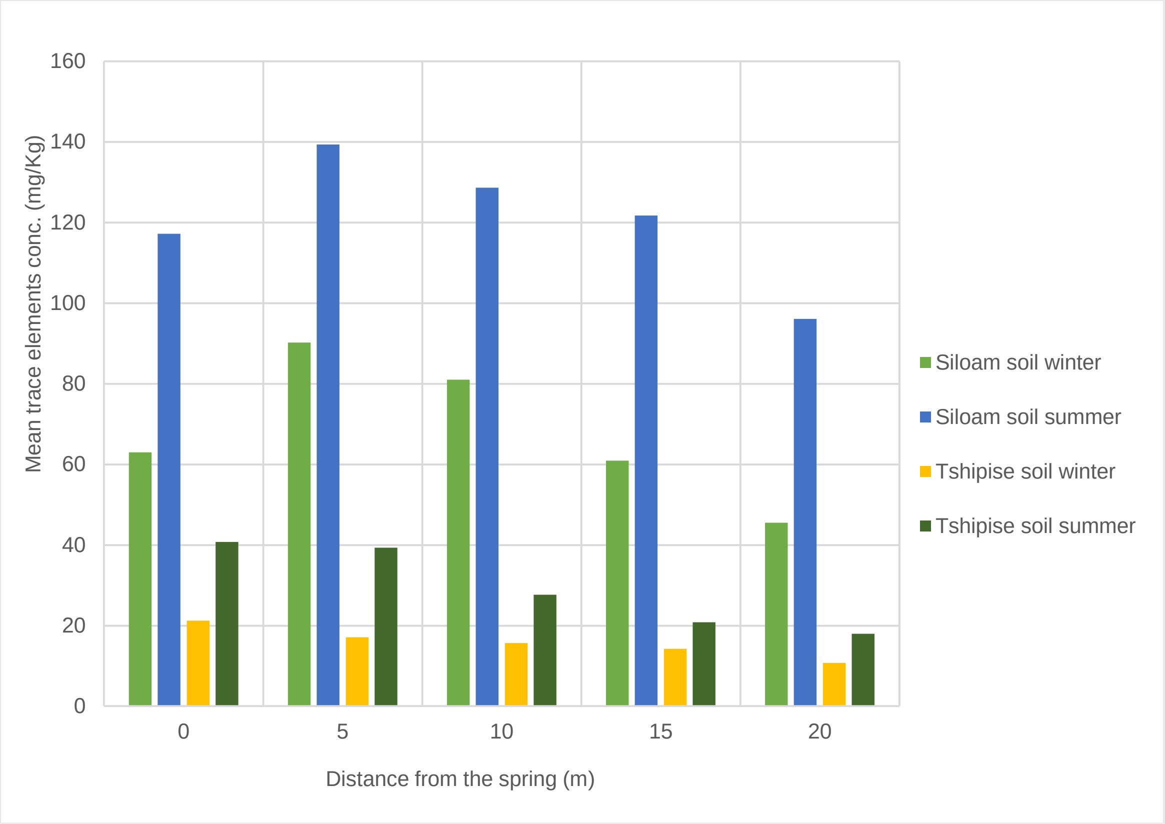


Figure 4.7: Mean concentrations of the trace elements in soil at different distances in the study areas

Figure 4.8: Chicken washing near the geothermal spring at Siloam

Aside from sampling points SS2 and SS3 (Siloam), which have higher soil pH, SOM, SWR values than the closest sampling point SS1. Hence, there is more trace elements absorption at those points (SS2 and SS3) than point SS1. The SOM serves as a reservoir of nutrients, trace elements and water in the soil, aids in reducing compaction and surface crusting, and increases water infiltration into the soil. Organic matter has many negative charges due to the dissociation of organic acids, which have high affinity to adsorb metal cations and reduce their availability (Basta *et al.*, 2005; Vangheluwe *et al.*, 2005). The SWR ranging from 38.22% – 61.28% predicts the soil texture of both sites as clay and clay loam for Siloam and Tshipise. Although, clay is more dominant at Siloam. This also accounts for the adsorption and retention capacity of the trace elements in the soil. Soil pH shows that trace elements are readily available in alkaline medium (ranging from 7.64 – 6.58 and 7.68 – 7.33 at Siloam and Tshipise, respectively). That is, a deduction in acidity reduces the trace elements concentrations in the soil (Adamu *et al.*, 2011). The number of negatively charged binding sites for cations is therefore dependent on the soil pH, which implies an increase in pH promotes the sorption of trace elements (Vanghelume *et al.*, 2005).

4.3.2 Chemical composition of the soil

Table 4.5 shows the chemical composition of the surface soil at sites (Siloam, Tshipise and control) and the Piper diagram was used to depict the composition as well as the seasonal variation in the soil. The EC and TDS values were high at SS1 and ST1 (Siloam and Tshipise) indicating more dissolved solids at that point. Comparing EC and TDS values for sites SS1 and ST1 with the control for winter and summer, EC (1920 µS/cm > 1730 µS/cm; 2550 µS/cm > 1140 µS/cm and 670 µS/cm > 650 µS/cm) and TDS (1240 mg/L > 1140 mg/L; 1630 mg/L > 729 mg/L and 424 mg/L > 420 mg/L) for Siloam, Tshipise and control respectively, were higher in winter than in summer season and this could be as a result of leaching away of top soil during rainy season (summer) resulting in the loss of minerals to the water. This causes significant differences in the EC and TDS values between summer and winter as reflected in Table 4.5 particularly where the soil is uneven (slightly inclined in Tshipise). Comparing the EC and TDS values obtained from SS1 and ST1 with those of the control site having 670 and 650 µS/cm (EC) and 424 and 420 mg/L (TDS) for winter and summer, respectively, show less values for the control site. This implies that there are more dissolved solids in the neighbouring soils of the geothermal springs compared to the soil from non-geothermal source. Since the EC values were less than 2 mmho/cm, the soil samples have low salt accumulation which will not affect plant growth (Tree Fruit research & Extension center, 2004).

Generally, the EC and TDS values were not evenly distributed from SS1 – SS5 and ST1 – ST5 at Siloam and Tshipise, respectively. EC and TDS values fluctuate with the distance away from spring showing non-uniform distribution of dissolved solids in the soil (Table 4.5). This implies that EC and TDS could not be used as indicators for availability of trace elements in the soil with distance.

From Figures 4.9 and 4.10, the piper diagram predicts the major chemical composition of soil (Siloam, Tshipise and control) as Na-Cl in both winter and summer season at the closest point (SS1 and ST1 to the geothermal spring). Along the distance (SS1 – SS5 for Siloam; ST1 – ST5 for Tshipise), the chemical composition changes to Ca-Cl in both sites due to cation exchange processes in the soil. The dominant cations are Na^+ and Ca^{2+} reflecting the soil pedogenesis (basalt). The figures show clear change in the chemical composition of the surface soils from Na-Cl to Ca-Cl along the distance away from the geothermal spring at both sites. Seasonal variation follows the same trend in both seasons at Siloam and Tshipise. However, higher concentrations of the composition were obtained in the winter than summer season. The chemical composition at the control site was Na-Cl showing similarities with compositions at SS1 and ST1, hence falls under the Soutpansberg region (Salt pan mountains).

Table 4.5: Chemical composition of soils at control site, Siloam and Tshipise

SEASON	Sample code	EC µS/cm	TDS mg/L	Ca mg/Kg	Mg mg/Kg	Na mg/Kg	K mg/Kg	SO_4 mg/Kg	F mg/Kg	Cl mg/Kg	NO_3 mg/Kg	HCO_3 mg/Kg
WINTER	SS1	1940.00	1240.00	172.47	29.02	239.4	22.4	205.24	1.24	257.49	25.39	4.40
	SS2	460.00	294.00	49.86	15.12	31.84	11.41	30.97	0.80	35.07	2.12	1.20
	SS3	430.00	275.00	44.37	16.18	25.47	5.39	38.24	0.69	46.23	0.39	1.30
	SS4	680.00	435.00	68.87	25.18	32.35	7.61	34.41	0.53	95.64	1.11	1.36
	SS5	780.00	499.00	121.01	31.75	27.34	10.63	33.84	0.52	96.19	0.53	4.63
SUMMER	SS1	1780.00	1140.00	15.29	11.80	170.06	10.24	171.87	3.16	379.53	151.1	1.95
	SS2	800.00	512.00	36.64	11.28	53.72	6.19	61.49	18.4	168.00	21.87	0.87
	SS3	590.00	377.00	31.74	13.44	19.19	6.81	68.75	2.19	94.67	18.45	1.76
	SS4	690.00	429.00	41.36	16.82	20.59	8.67	59.32	0.86	103.15	61.8	1.05
	SS5	1030.00	659.00	77.04	20.80	27.87	10.03	91.67	3.73	151.34	87.11	0.71
WINTER	ST1	2550.00	1630.00	111.11	61.53	423.87	28.48	159.61	0.73	216.68	32.86	3.44
	ST2	790.00	550.00	75.13	40.28	52.61	11.20	22.25	0.65	14.91	13.07	1.87
	ST3	510.00	326.00	37.94	22.33	60.74	8.12	18.8	0.65	25.14	6.61	1.10
	ST4	450.00	288.00	46.38	22.03	33.84	8.80	15.57	0.74	10.29	17.19	1.27
	ST5	500.00	320.00	52.55	22.79	37.74	15.66	16.34	0.64	11.63	18.97	1.98
SUMMER	ST1	1140.00	729.00	39.37	17.97	130.46	9.81	67.64	2.57	82.63	189.55	1.16
	ST2	470.00	301.00	15.29	12.67	13.43	7.83	15.5	0.76	31.55	134.07	0.99
	ST3	340.00	218.00	10.15	8.16	10.11	5.23	9.88	0.77	23.24	71.8	0.28
	ST4	320.00	205.00	13.54	6.33	9.75	6.23	7.06	0.84	11.51	53.64	0.26
	ST5	393.70	252.00	17.87	8.25	23.12	8.15	18.08	1.03	28.16	65.21	0.54
CONTROL	WSC	670.00	424.00	39.18	11.78	8.86	22.06	21.80	0.27	15.00	3.08	0.66
	SSC	650.00	420.00	39.10	11.70	6.90	21.70	21.76	0.21	14.80	3.08	0.64

WSC = winter control, SSC = summer control

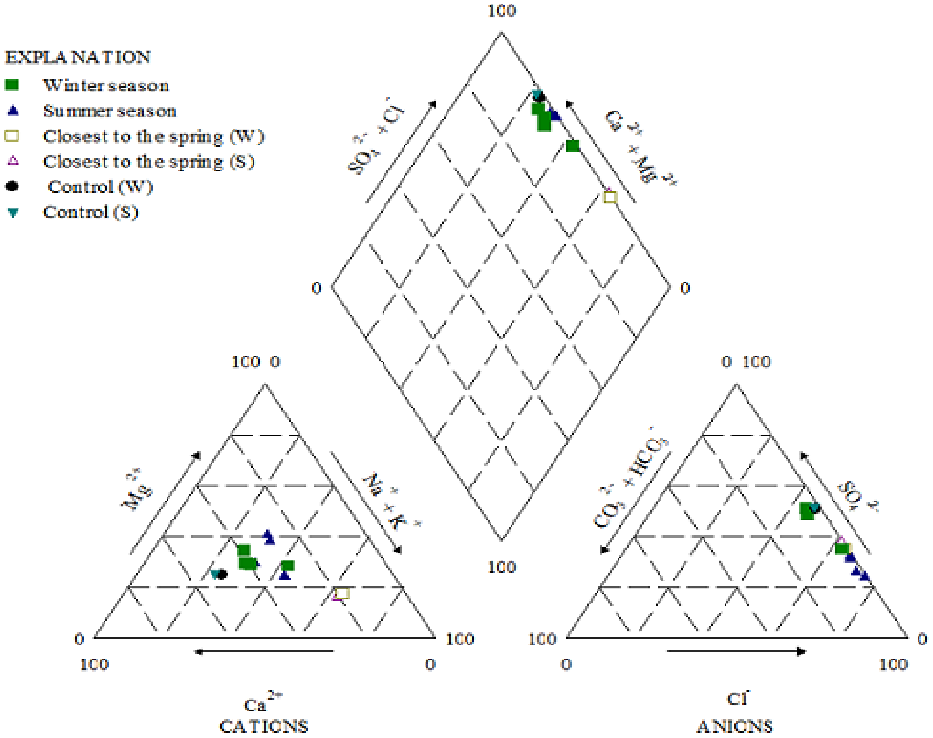


Figure 4.9: Piper diagram showing the chemical composition of Tshipise and control soils

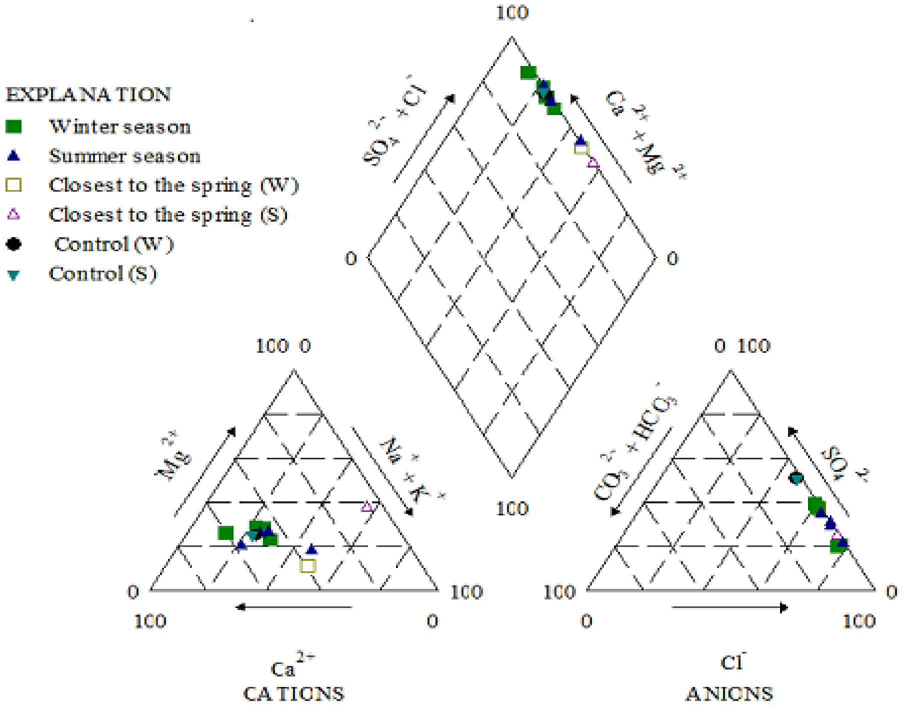


Figure 4.10: Piper diagram showing the chemical composition of Siloam and control soils

The concentrations of F^- and NO_3^- were not accounted for in the piper diagram. At Siloam soil, F^- concentrations were high (0.84 – 18.4 > 0.54 – 1.24 mg/Kg) particularly in summer compared to winter season. This could be attributed to elevated F^- concentrations from the geothermal springs and more rainfall in summer season. F^- concentrations at sampling points (SS2 & SS5) were higher (18.4 & 3.73 mg/Kg) than at sampling point SS1, particularly in winter, which slightly conforms to indicator's prediction. At Tshipise, the F^- concentrations were not evenly distributed and hence, do not conform to the indicators. The concentration of F^- at the control site was less (0.27 mg/Kg for winter and 0.21 mg/Kg for summer) compared to any sampling points at Siloam and Tshipise soil for both seasons. This also emphasises on the effect of the geothermal spring's water on their surrounding soil.

The concentrations of NO_3^- were not evenly distributed in the sampled points at both study sites, having the highest concentrations at point SS1 and ST1 (25.39; 151.1 and 32.86; 189.55 mg/Kg for winter and summer, respectively). Contrary to F^- concentrations, the concentration of NO_3^- were higher in summer than winter, owing to more dissolution from rainfall to aid the nitrification processes in the soil. Comparing with control site, the NO_3^- concentrations at any sampled points from both sites were higher than the concentration at control site (3.08 mg/Kg) for both seasons.

4.3.3 Trace element concentrations in soil

Trace elements found in the surrounding soil close to the geothermal spring were as a result of the geothermal water and the soil pedogenesis. As explained earlier, geothermal water contaminates the soil with substantial quantity of trace elements absorbed as water flows and get utilised in the surroundings. Tables 4.6 and 4.7 show descriptive summary of trace elements concentrations at Siloam, Tshipise and control soils for both winter and summer season. Trace elements concentrations vary with distance away from the geothermal spring (Figures 4.11 and 4.12). Indicator graph (Figure 4.6) also shows the same spatial variation. This implies there is a strong correlation between the indicators (Soil pH, SOM and SWR) and trace elements availability. However, trace elements concentrations depend greatly on the indicators for their availability and mobility in the soil. The trace elements concentrations at the control site shows little variation in winter and summer seasons, having mean trace elements concentrations values of 20.06 to 20.28 mg/Kg, respectively.

Table 4.6: Descriptive summary of trace elements concentrations at Siloam and control soils

				Winter season					Summer season				
	DNHPD,	Control W	Control S	SS1	SS2	SS3	SS4	SS5	SS1	SS2	SS3	SS4	SS5
Elements	1991	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
Li		3.56	3.60	4.63	4.88	3.92	2.92	2.80	11.14	11.29	9.26	8.31	9.54
Be		0.85	0.09	0.60	0.74	0.66	0.52	0.46	0.79	0.89	0.72	0.72	0.72
B		0.30	0.32	0.29	0.88	0.89	0.32	0.85	0.75	1.77	0.79	0.65	1.91
Ti		90.40	90.40	89.96	222.04	127.32	95.98	90.42	1045.70	1291.25	1114.06	1076.04	897.67
V		34.40	34.80	92.07	156.40	149.35	121.40	115.89	141.43	194.21	172.69	185.04	190.02
Cr	80.00	54.00	58.46	46.70	**83.53**	**80.55**	62.09	54.80	72.48	**111.63**	**97.64**	**97.69**	**96.22**
Mn		129.00	130.00	841.26	1445.00	1375.00	1052.00	733.72	978.10	**1445.00**	**1239.00**	**1169.00**	**860.41**
Co	20.00	19.10	19.14	**29.87**	**48.20**	**45.41**	**35.84**	**29.10**	**36.70**	**49.51**	**43.11**	**41.87**	**36.35**
Ni	50.00	25.03	25.08	35.80	**82.86**	**77.10**	40.18	32.84	49.07	**67.30**	**53.28**	49.93	41.73
Cu	100.00	70.46	70.56	73.92	**116.52**	**109.43**	85.89	72.10	**222.97**	**310.96**	**263.10**	**256.45**	**238.55**
Zn	185.00	50.19	50.23	**225.08**	123.93	52.82	40.59	74.87	364.77	107.32	80.70	165.47	86.50
As	2.00	1.39	1.39	**0.76**	0.90	0.81	0.81	0.76	0.75	0.56	0.55	0.49	0.78
Se		1.39	1.43	0.55	0.80	0.79	0.55	0.61	0.64	0.95	0.85	0.88	0.76
Rb		16.39	16.43	16.07	16.43	11.86	5.76	5.43	19.49	7.72	6.54	5.64	6.18
Sr		11.64	11.68	20.38	26.84	24.94	19.43	17.19	28.69	36.85	27.16	26.85	26.96
Mo		0.12	0.16	0.18	0.16	0.16	0.15	0.17	0.11	0.07	0.08	0.07	0.07
Cd	2.00	0.23	0.25	0.17	0.16	0.07	0.06	0.07	0.13	0.09	0.08	0.07	0.10
Sn		0.20	0.26	0.17	0.14	0.07	0.05	0.07	0.29	0.23	0.22	0.16	0.12
Sb		0.90	1.00	1.75	0.88	1.16	1.46	1.28	0.01	0.01	0.01	0.01	0.01
Cs		0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.31	0.23	0.22	0.01	0.01
Ba		0.40	0.48	0.41	0.36	0.31	0.25	0.20	208.98	241.92	191.36	202.05	170.76
La		13.34	13.43	144.54	182.71	168.45	128.93	111.09	13.20	14.33	12.24	12.19	12.34
W		0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.03	0.02	0.01	0.01	0.01
Hg		0.03	0.05	0.04	0.08	0.12	0.06	0.10	0.06	0.05	0.03	0.05	0.04
Tl		0.11	0.11	0.04	0.07	0.06	0.05	0.04	0.04	0.05	0.04	0.04	0.04
Pb	56.00	21.40	21.42	**138.44**	10.75	8.92	10.30	13.48	**84.18**	7.30	7.33	8.38	12.71
Bi		0.05	0.07	0.07	0.03	0.02	0.02	0.02	0.12	0.02	0.01	0.01	0.02
U		0.20	0.38	0.10	0.12	0.12	0.11	0.13	0.10	0.11	0.10	0.10	0.12
Count		28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00
Mean		**20.06**	**20.28**	**63.00**	**90.19**	**80.01**	**60.92**	**45.53**	**117.18**	**139.34**	**128.61**	**121.73**	**96.09**
STDdev		35.57	32.90	162.66	273.09	258.80	198.11	139.13	267.34	356.81	306.70	294.12	230.19
STD.Error		6.27	6.33	30.74	51.61	48.91	37.44	26.29	50.52	67.43	57.96	55.29	43.50

W = winter, S = summer

Bold data are above the guideline for maximum permissible trace elements concentrations in agricultural soils in South Africa (DNHPD, 1991) (mg/Kg) as well as the mean value.

Table 4.7: Descriptive summary of trace elements concentrations at Tshipise and control soils

				Winter season					Summer season				
	DNHPD,	Control W	Control S	ST1	ST2	ST3	ST4	ST5	ST1	ST2	ST3	ST4	ST5
Elements	1991	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
Li		3.56	3.60	3.81	2.37	2.72	2.32	2.22	6.28	1.02	3.74	4.04	3.23
Be		0.85	0.09	0.19	0.19	0.21	0.17	0.14	0.24	0.21	0.20	0.23	0.21
B		0.30	0.32	3.03	1.94	1.31	0.59	0.54	3.77	1.59	1.71	0.61	0.55
Ti		90.40	90.40	168.77	110.30	110.05	63.53	55.81	705.12	527.23	463.85	266.59	246.20
V		34.40	34.80	17.54	16.20	14.14	12.98	9.89	23.32	17.18	16.80	15.85	13.14
Cr	80.00	54.00	58.46	32.55	26.34	27.99	23.63	23.21	44.28	35.98	32.61	33.18	32.43
Mn		129.00	130.00	174.94	143.36	131.05	133.97	101.74	178.46	105.40	116.74	121.18	112.90
Co	20.00	19.10	19.14	3.98	3.75	3.53	3.35	2.53	3.22	2.11	2.20	2.57	2.17
Ni	50.00	25.03	25.08	23.15	21.82	21.90	19.45	16.75	1.81	0.01	0.01	0.01	0.01
Cu	100.00	70.46	70.56	11.39	8.82	7.85	8.07	5.26	19.34	8.79	10.29	10.22	9.18
Zn	185.00	50.19	50.23	50.08	35.86	26.29	52.56	22.11	53.60	332.69	67.22	32.51	22.22
As	2.00	1.39	1.39	0.65	0.56	0.56	0.48	0.35	0.56	0.53	0.45	0.45	0.42
Se		1.39	1.43	0.43	0.22	0.37	0.25	0.17	0.44	0.23	0.20	0.24	0.18
Rb		16.39	16.43	7.13	3.76	3.97	2.88	2.73	6.54	4.34	2.93	3.16	2.40
Sr		11.64	11.68	57.73	69.31	52.11	43.24	33.57	51.79	34.89	27.11	56.81	31.87
Mo		0.12	0.16	0.17	0.13	0.10	0.07	0.05	0.17	0.11	0.11	0.16	0.10
Cd	2.00	0.23	0.25	0.06	0.06	0.04	0.05	0.03	0.07	0.04	0.05	0.03	0.05
Sn		0.20	0.26	0.06	0.06	0.04	0.04	0.02	0.19	0.15	0.17	0.25	0.51
Sb		0.90	1.00	1.21	1.10	1.65	1.74	2.19	0.01	0.00	0.01	0.01	0.03
Cs		0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.49	0.39	0.01	0.01	0.16
Ba		0.40	0.48	0.61	0.32	0.40	0.29	0.27	30.29	21.24	19.60	26.60	19.88
La		13.34	13.43	34.37	28.84	29.65	27.09	19.19	9.30	5.99	7.59	5.85	2.86
W		0.01	0.01	0.02	0.03	0.03	0.03	0.02	0.01	0.01	0.01	0.01	0.04
Hg		0.03	0.05	0.07	0.04	0.07	0.01	0.04	0.12	0.02	0.02	0.03	0.02
Tl		0.11	0.11	0.03	0.02	0.04	0.02	0.02	0.02	0.02	0.01	0.02	0.01
Pb	56.00	21.40	21.42	3.07	2.49	3.58	2.82	2.33	2.26	1.33	1.50	1.60	1.89
Bi		0.05	0.07	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.00	0.01	0.01
U		0.20	0.38	0.18	0.11	0.09	0.11	0.05	0.11	0.08	0.07	0.06	0.04
Count		28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00
Mean		**20.06**	**20.28**	**21.26**	**17.07**	**15.71**	**14.28**	**10.76**	**40.78**	**39.34**	**27.69**	**20.80**	**17.95**
STDdev		35.57	32.90	45.38	34.98	32.34	29.09	22.10	134.99	115.44	89.13	54.49	50.03
STD.Error		6.27	6.33	8.58	6.61	6.11	5.50	4.18	25.51	21.82	16.84	10.30	9.45

W = winter, S = summer

Bold data are above the guideline for maximum permissible trace elements concentrations in agricultural soils in South Africa (DNHPD, 1991) (mg/Kg) as well as the mean value

As seen in Figure 4.6A, sampling points SS2 & SS3 (Siloam) have higher values for pH, SOM and SWR which also reflect on the mean trace elements concentrations at those points. The reason for this was explained earlier and hence more trace elements were obtained at that point (Figure 4.7). Generally, mean trace elements concentrations decrease with distance (Figures 4.11 and 4.12) as well as the indicators (Figures 4.6A and 4.6B). Figures 4.11 and 4.12 show clearly the effect of seasonal variation in the availability of the trace elements in the soil. The trace elements concentrations were higher in summer compared to winter (Figures 4.11 and 4.12) even though, the EC and TDS values were higher in winter compared to summer (Table 4.5). This implies that EC and TDS could only predict the presence of dissolved solids but they are not indicators to quantify the concentration of what available in a media.

At Siloam, the mean trace elements concentrations is negatively weak correlated to the distance from the geothermal spring ($R^2 = 0.35$; 0.34 for summer and winter seasons, respectively: $P < 0.05$) (Figure 4.11). At Tshipise on the other hand, the mean trace elements concentrations is negatively correlated (strong) to the distance away from the spring ($R^2 = 0.94$; 0.96 for the summer and winter seasons, respectively: $P < 0.05$) (Figure 4.12). This implies that the availability of trace elements decreases with the distance from the geothermal spring. That is, more trace elements should be available at SS1 and ST1 except for SS2 and SS3, which have more trace elements compared to the other points due to reasons explained earlier (Figures 4.7 and 4.8).

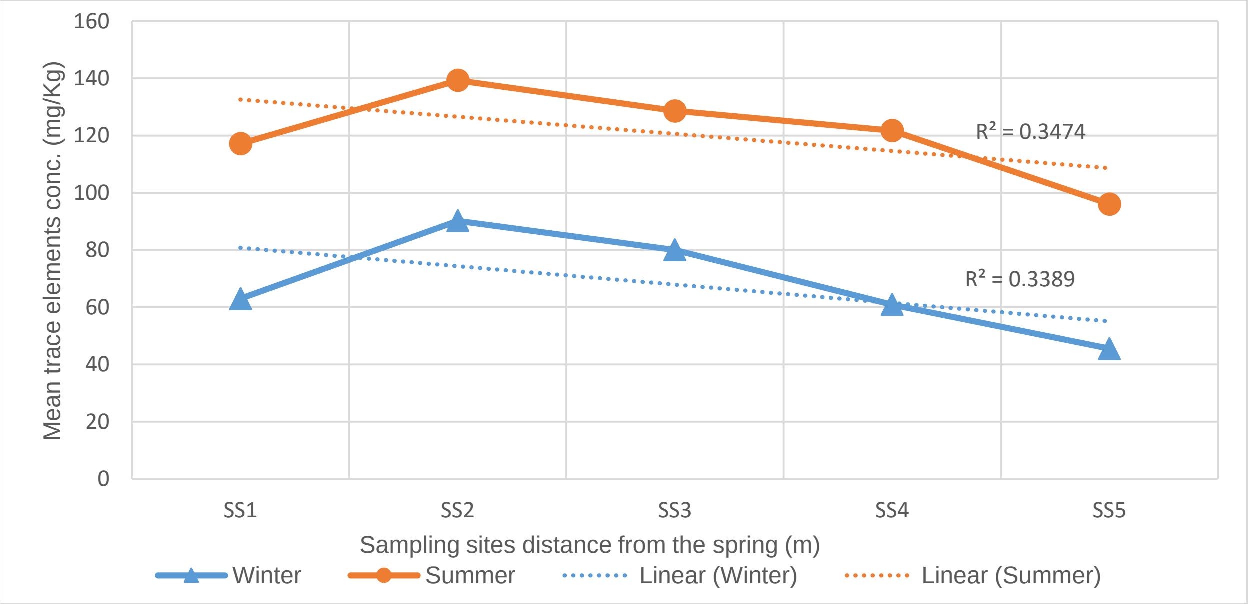


Figure 4.11: Horizontal status of mean trace element concentrations at Siloam soil

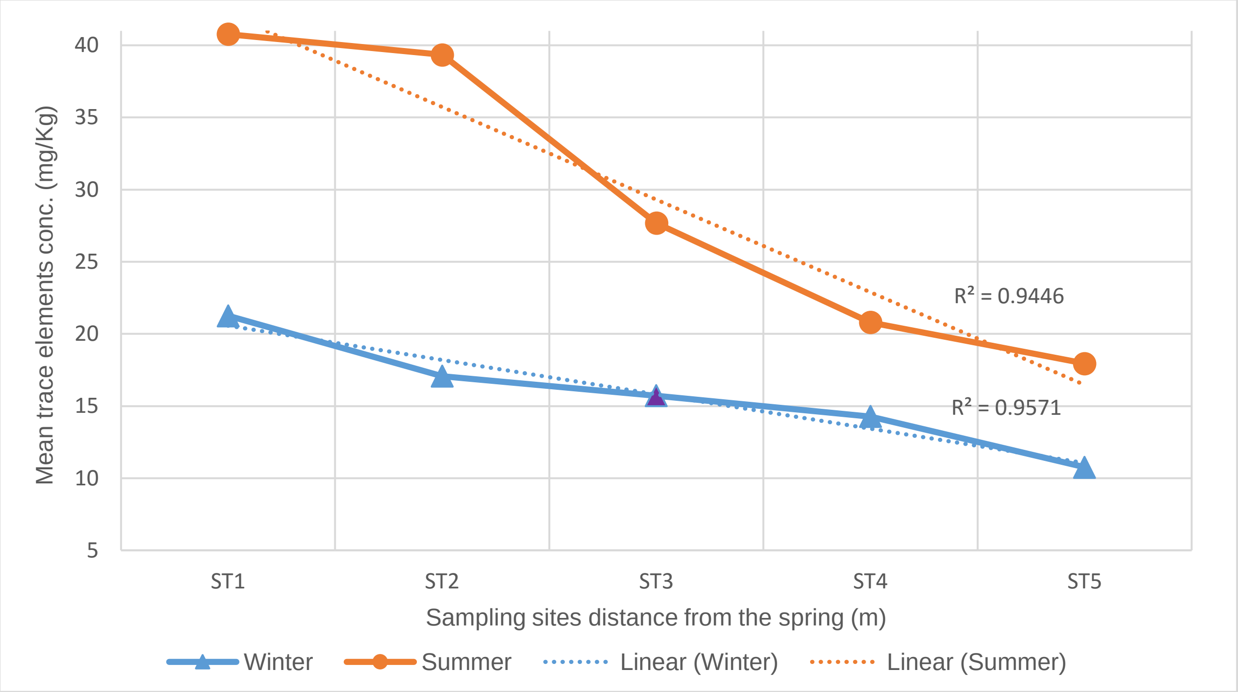


Figure 4.12: Horizontal status of mean trace element concentrations at Tshipise soil

Most of the trace elements show high positive correlation coefficient greater than 0.5, which implies that there is a strong correlation between the trace elements and the indicators (Table 4.8). This strong relationship with the indicator could possibly result due to availability of the trace elements in the soil. Statistical analysis (Table 4.8) shows that most of the trace elements in soil (Siloam and Tshipise) are positively correlated with at least one of the indicators (soil pH, %SOM and %SWR) except for a few trace elements such as Sr, Sb, Cs at Tshipise and B, Hg, U at Siloam showing negative correlation. Although, B and Ba at Tshipise and Li, V, Cr, Sb and Mo at Siloam are less correlated to one of the indicators. De Haan (1993) and Siegel (2002) reported that there is no correlation between organic matter and the levels of trace elements in the soil, which this study has disapproved. However, these positive correlations between trace elements and soil properties called indicators (soil pH, %SOM and %SWR) may be an indication of their influence on trace elements dispersion and concentration in soils (Adamu *et al*., 2011).

Table 4.8: Pearson correlation matrix of the trace elements and the indicators at Siloam and Tshipise soils

Correlation matrix	**Tshipise**			**Siloam**		
	Soil pH	% SOM	% SWR	Soil pH	% SOM	% SWR
Li	**0.597**	0.204	0.307	0.339	-0.039	-0.098
Be	**0.831**	**0.999**	**0.98**	**0.594**	**0.909**	**0.926**
B	0.415	-0.117	0.007	-0.501	-0.059	-0.044
Ti	**0.575**	0.072	0.198	0.153	**0.587**	**0.628**
V	**0.785**	**0.993**	**0.958**	-0.168	0.291	0.355
Cr	**0.888**	**0.986**	**0.975**	-0.022	0.418	0.48
Mn	**0.803**	**0.995**	**0.966**	0.27	**0.644**	**0.701**
Co	**0.773**	**0.991**	**0.954**	0.188	**0.595**	**0.653**
Ni	**0.944**	**0.973**	**0.995**	0.21	**0.635**	**0.677**
Cu	**0.79**	**0.994**	**0.961**	0.191	**0.605**	**0.66**
Zn	**0.802**	**0.831**	**0.902**	**0.691**	**0.538**	0.466
As	**0.989**	**0.822**	**0.906**	0.139	**0.533**	**0.598**
Se	**0.92**	**0.899**	**0.934**	0.002	0.465	0.496
Rb	**0.79**	0.44	**0.531**	**0.799**	**0.935**	**0.905**
Sr	-0.176	-0.621	-0.505	0.44	**0.81**	**0.842**
Mo	**0.956**	**0.66**	**0.751**	0.271	0.101	0.006
Cd	**0.922**	**0.716**	**0.828**	**0.7**	**0.735**	**0.693**
Sn	**0.939**	**0.695**	**0.802**	**0.714**	**0.703**	**0.647**
Sb	-0.801	-0.438	-0.568	0.358	-0.135	-0.189
Cs	-0.268	-0.56	-0.579	**0.756**	**0.921**	**0.893**
Ba	0.125	-0.365	-0.248	**0.939**	**0.932**	**0.897**
La	**0.827**	**0.998**	**0.977**	**0.559**	**0.884**	**0.907**
W	-0.32	-0.381	-0.293	-0.096	-0.356	-0.441
Hg	**0.866**	**0.836**	**0.813**	-0.578	-0.254	-0.233
Tl	**0.896**	**0.916**	**0.922**	0.156	**0.577**	**0.639**
Pb	**0.769**	**0.989**	**0.952**	**0.702**	0.377	0.3
Bi	**0.856**	**0.693**	**0.74**	**0.77**	**0.516**	0.444
U	**0.723**	0.317	0.473	-0.859	-0.522	-0.498
Soil pH	1	**0.849**	**0.912**	1	**0.874**	**0.849**
% SOM	**0.849**	1	**0.981**	**0.874**	1	**0.995**
% SWR	**0.912**	**0.981**	1	**0.849**	**0.995**	1

Note: In bold are high positive scores (>0.50) at significance level alpha = 0.05

Seasonal variations at both sites at the closest distance to the geothermal spring (SS1 and ST1) (Figures 4.13 and 4.14) show how each trace element in the soil varies with the season. In summer, 71.43% of the total trace elements (Li, Be, B, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Se, Rb, Sr, Sn, Cs, Ba, W, Hg, Bi) were higher in concentrations than winter; 17.85% of the total trace elements (Mo,Cd, Sb, La, Pb) were higher in concentrations in winter than in summer while 10.72% of the total trace elements (As, Tl, U) remained constant in concentrations in both seasons at Siloam (Figure 4.13). At Tshipise, 46.43% of the total trace elements (Li, Be, B, Ti, V, Cr, Cu, Zn, Cd, Sn, Cs, Ba, Hg) were higher in concentrations in summer than in winter; 42.86% of the total trace elements (Co, Ni, As, Sr, Rb, Sr, Sb, La, W, Tl, Pb, Bi, U) were higher in concentrations in winter than in summer and 10.71% (Mn, Se and Mo) remained constant in concentrations during both seasons (Figure 4.14).

The findings of the study were compared with South African Guidelines for maximum permissible trace element concentrations in agricultural soils, which are: 2 mg/Kg As, 20 mg/Kg Co, 80 mg/Kg Cr, 2mg/Kg Cd, 50 mg/Kg Ni, 56 mg/Kg Pb, 185 mg/Kg Zn and 100 mg/Kg Cu (DNHPD, 1991). Soils at Tshipise were within the maximum permissible trace element concentrations, owing to low level of trace elements from the geothermal spring as well as its utilisation resulting in less concentrations of the trace elements, as it is found at a resort.

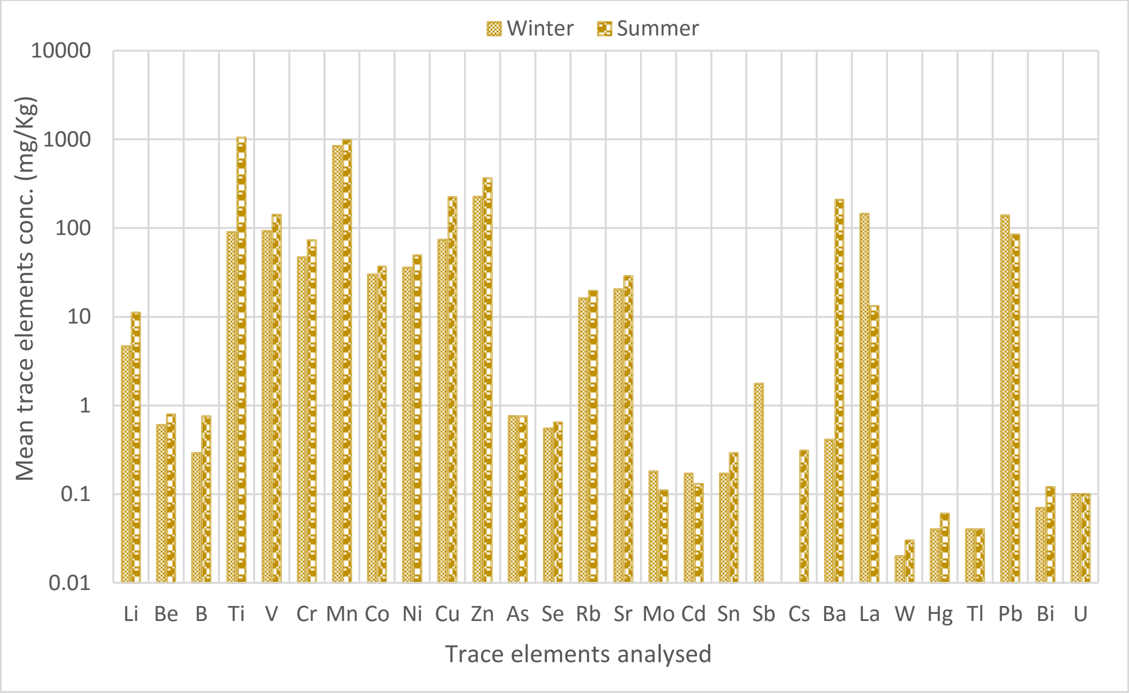


Figure 4.13: Seasonal variation in the trace element concentrations in Siloam soil

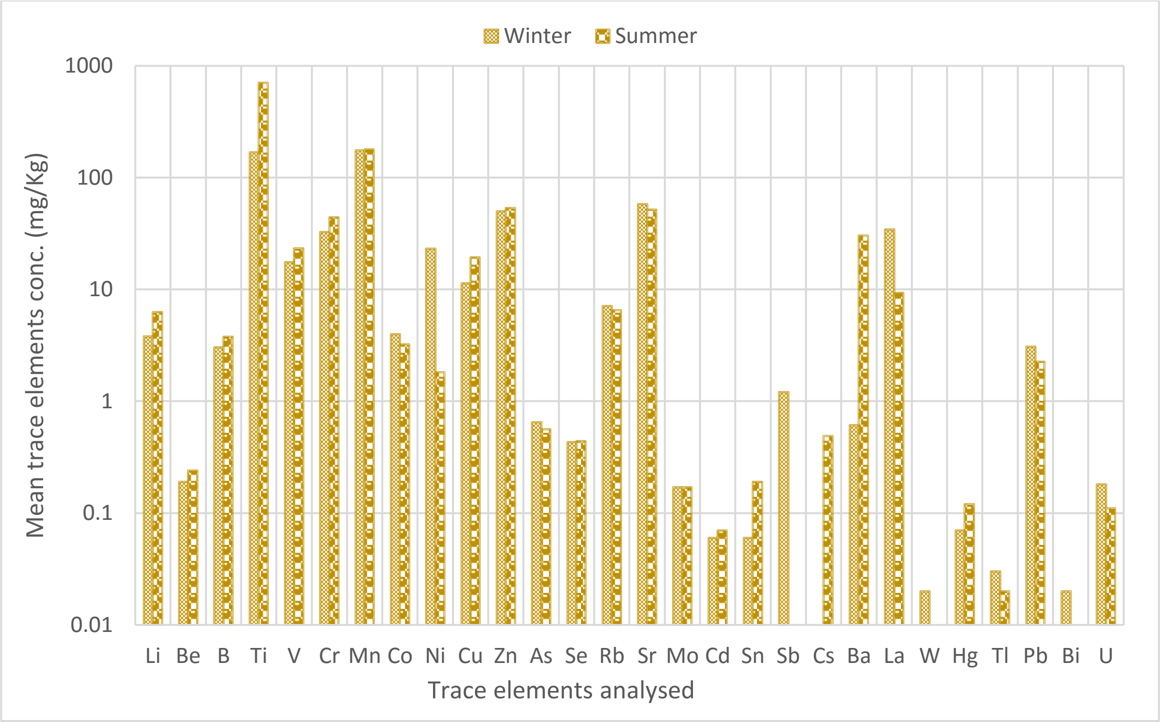


Figure 4.14: Seasonal variation in the trace element concentrations in Tshipise soil

At Siloam, the trace element concentrations in soil were higher in Cr, Co, Ni, Cu, Zn and Pb, compared to South African maximum permissible limits for agricultural soils. These could be attributed to more trace element concentrations from the geothermal springs as well as higher utilisation of spring water on the soil, which leads to contamination. Comparison of the trace elements concentrations from both sites with the control site trace elements concentrations, shows that the neighbouring soils from the geothermal springs were partially or moderately contaminated with trace elements, which enter the human body via the food chain.

4.3.4 Seasonal variation of trace element concentrations on the soils

Statistically, Tables 4.9A and 4.9B show that there are significant differences in the trace elements concentrations in winter and summer ($p < 0.05$). Each trace element differs (in row) in concentration during the two seasons which implies that seasonal variation plays an important role in the availability of trace elements. This also validates the finding that more concentrations of trace elements are available in the summer season compared to the winter season owing to the rainfall and anthropogenic factors, which leads to more decomposition of organic matter and dissolution of rocks.

Table 4.9: ANOVA for Siloam and Tshipise soils

A - Siloam

Source of Variation	SS	df	MS	F	P-value	F critical
Rows	407988	27	15110.67	2.921806	**0.003483**	1.904823
Columns	5334.621	1	5334.621	1.031505	0.318821	4.210008
Error	139635.5	27	5171.687			
Total	552958.2	55				

B - Tshipise

Source of Variation	SS	df	MS	F	P-value	F critical
Rows	2164735	27	80175.38	4.515348	**0.0001**	1.904823
Columns	41102.57	1	41102.57	2.314831	0.139772	4.210008
Error	479417.1	27	17756.19			
Total	2685255	55				

4.4 Vegetation around the geothermal springs

4.4.1 Chemical compositions of *Acacia robusta* and *Mangifera indica*

The TDS values for *Acacia robusta* (44.8 < 574 ppm in winter; 65.8 < 720 ppm in summer) were higher in the leaves compared to the bark, which implies that there are more total dissolved solids in the leaves than the barks (Table 4.10). On the contrary, there are more essential minerals in the barks of the plants for both sites than the leaves. This is due to transpiration of the minerals from the root system via the bark to the leaves. The TDS values for *Mangifera indica* (214 > 179 ppm for winter; 230 > 190 ppm for winter) were higher in the bark compared to the leaves, which implies more essential minerals in the bark than the leaves (Table 4.9). Comparing both seasons, TDS values were higher in *Acacia robusta* (65.8 > 44.8 ppm for bark; 720 > 572 ppm for leaves) and *Mangifera indica* (230 > 214 ppm for bark; 190 > 179 ppm for leaves) in summer compared to winter season. This could be as a result of higher rainfall which promotes the dissolution of minerals. Although, the TDS increases from winter to summer season, the mean essential minerals decrease (1175.72 – 864.39 mg/Kg barks and 1022 – 644.46 mg/Kg leaves of *Acacia robusta*; 1295.03 – 714.59 mg/Kg barks and 890.05 – 658.24 mg/Kg leaves of *Magnifera indica)*. This implies that the TDS does not really predict the availability of essential minerals in plants as in the case of water and soil. However, it is possible that the essential minerals were utilised more in summer because it is prior to the fruit formation (Ojekunle *et al*., 2014).

Table 4.10: Essential chemical composition of *Acacia robusta* and *Mangifera indica*

	Acacia robusta				A. robusta control				Mangifera indica				M. indica control			
	Bark	Leaf	Bark	Leaf	Bark	Leaf	Bark	Leaf	Bark	Leaf	Bark	Leaf	Bark	Leaf	Bark	Leaf
EC (µS/cm)	70	900	103	1130	530	285	560	296	335	280	359	297	325	235	346	256
TDS (mg/L)	44.8	574	65.8	720	339	182	208	150	214	179	230	190	358	189	221	164
Ca (mg/Kg)	2243	3533	2240	1260	218	180	212	178	2327	1198	4020	1900	242	200	264	245
Mg (mg/Kg)	197.1	274.8	231	246	16.7	23.9	19.2	23.54	358.13	159.1	231	202	76.6	8	84	13
Na (mg/Kg)	7411.3	580.5	530	1206	238	1131	422	325	649	944.37	665	1206	291	413	369	443
K (mg/Kg)	1344.7	70.93	49	2400	70.2	93.2	174	185	945.13	548.8	199	2400	41.6	50	87.9	96.3
Al (mg/Kg)	688.4	1571	695	467	1949	1014	958	407	1653	493.97	1555	614	1224	817	1369	916
Fe (mg/Kg)	439.5	895.6	5408	233	1441	696	854	759	1197	321.3	903	380	915	513	1016	621
F (mg/Kg)	0.01	0.06	N.D	N.D	1.2	1.79	1.8	1.5	N.D	N.D	N.D	N.D	15.9	13.7	12.69	15.26
Cl (mg/Kg)	160	931	1.37	46	11.8	30	15.2	23.1	330	750	1.11	4.67	0.04	0.07	1.02	3.02
NO3 (mg/Kg)	163.3	N.D	0.32	0.09	357	305	224	211	N.D	N.D	0.52	0.41	118	254	0.09	0.01
NO2 (mg/Kg)	52.7	N.D	0.08	0.09	199	14.2	154	36.1	N.D	102	0.33	0.67	107	N.D	95	0.65
SO4 (mg/Kg)	108	N.D	1.02	27.3	18.61	64.1	32.1	84	767	1732	0.53	4.91	756	348	865	421
PO4 (mg/Kg)	113.6	942	1.83	10.05	596	343	621	345	3173	2209	0.59	10.25	1335	1229	1423	1320
Mean (mg/Kg)	**1175.7**	**1023**	**864.4**	**644.5**	**426.4**	**324.68**	**307.28**	**214.85**	**1295**	**890.05**	**714.6**	**658.24**	**426.85**	**349.6**	**465.6**	**341.19**

N.D - Not detected

Table 4.10 shows the summary of the essential minerals found. This is interpreted using a piper diagram to ascertain the dominant chemical components of the plant. The major chemical component of *Mangifera indica* is Ca-Cl_2 for both winter and summer, respectively. The control has both leaves and barks dominated with Na-Cl and Ca-Cl_2 for winter and summer respectively. From Figure 4.15, bark and leaves are dominated with Ca-Cl_2 in summer and winter whereas the control bark has Ca-Cl_2 and leaf with Na-Cl for both seasons. This can be attributed to the cation exchange process between Na and Ca which are the dominating cations as a result of basalt from the soil. The chemical composition of the bark changes from Ca-Cl_2 to Na-Cl in leaf for both seasons. Other cations present are Al, Fe, K, Na and P, which is a metalloid needed for plant metabolism. Cl^- and SO_4^{2-} have a strong correlation (Durowoju *et al*., 2015) and other anions are PO_4, NO_3 and NO_2 which are major ingredients of fertilizers.

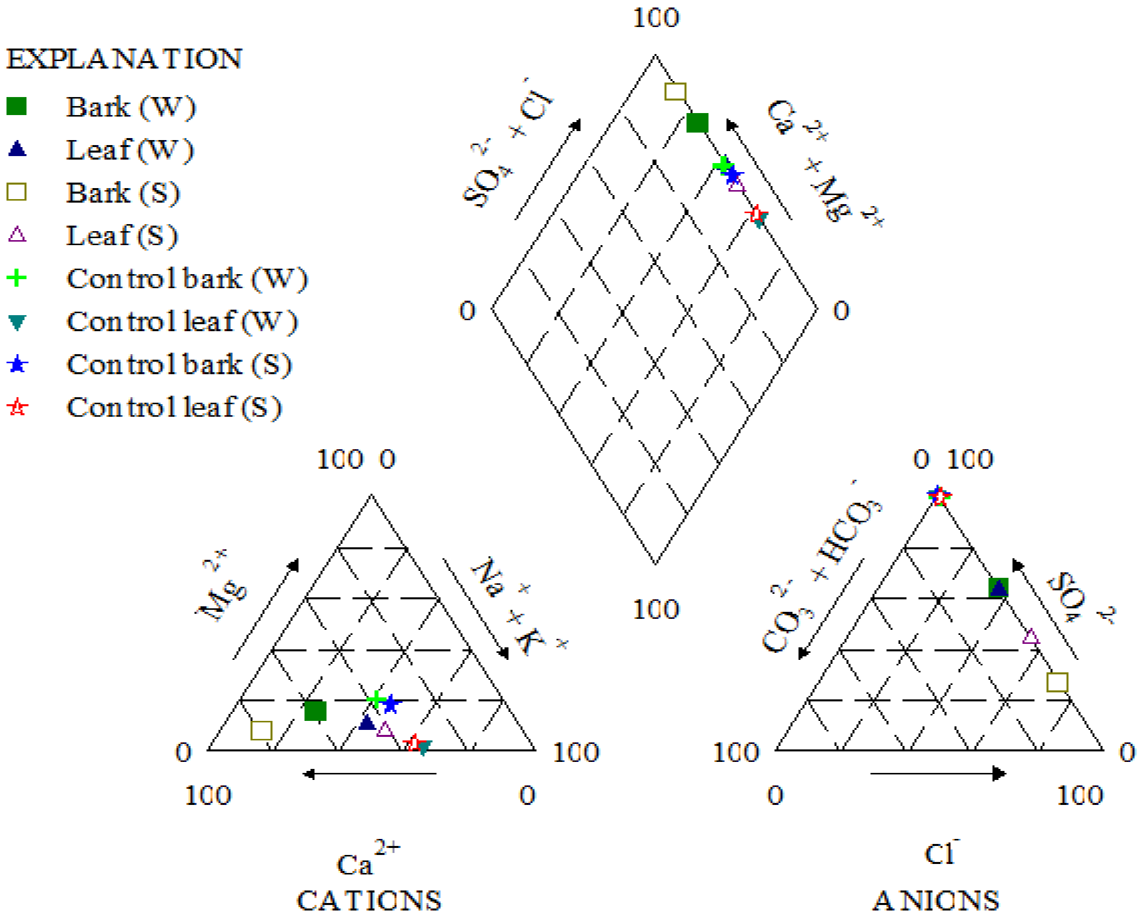


Figure 4.15: Piper diagram showing the chemical composition of *Mangifera indica* at Siloam and Riverside

The chemical composition of *Acacia robusta* is dominated by Ca-Cl_2 and Na-Cl in leaves and Na-Cl and Ca-Cl_2 in bark for winter and summer, respectively (Figure 4.16). For control, Ca-Cl_2 and Na-Cl in the bark for winter and summer, respectively, whereas Na-Cl in leaves for both season. The Ca-Cl_2 concentration is higher in the winter compared to the summer due to the rainfall which enhances dilution and dissolution of minerals. From the geothermal spring water, Na-Cl is dominant at SS1 (Siloam) but there is ion-exchange with Ca^{2+} making the chemical composition Ca-Cl_2. The Ca-Cl_2 is then transferred to the surrounding vegetation via transpiration from the root system to other parts leading to the chemical composition of *Mangifera indica* becoming Ca-Cl. At Tshipise spring, the dominant composition of the water is Na-HCO_3 and Ca-NaHCO_3 in winter and summer, respectively. There is anion exchange of HCO_3^- with Cl^-, making the soil Na-Cl at ST1 (closest distance) to cation exchange along the distance resulting in formation of Ca-Cl_2 owing to the concentration of Ca^{2+} present. Ca-Cl_2 was absorbed by the surrounding vegetation making *Acacia robusta* composition to be Ca-Cl_2.

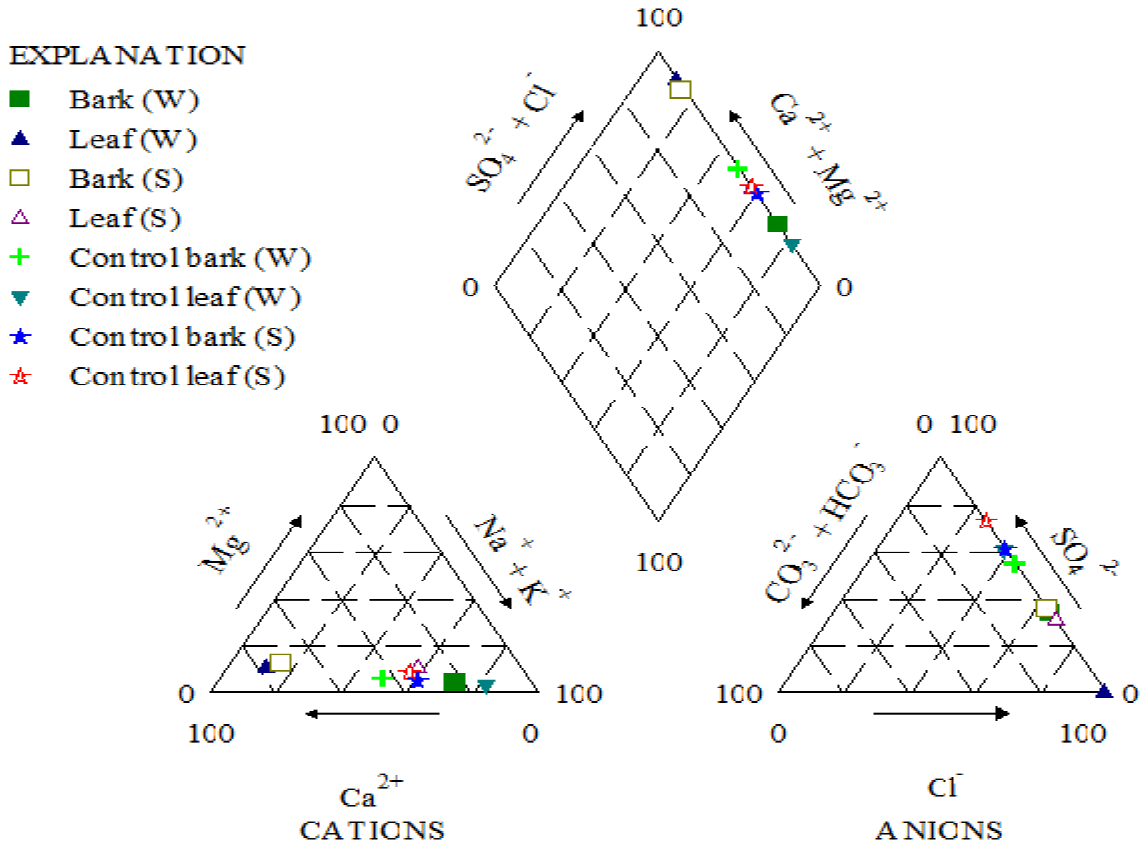


Figure 4.16: Piper diagram showing the chemical composition of *Acacia robusta* at Tshipise and Riverside

4.4.2 Trace element concentrations in *Acacia robusta* and *Mangifera indica*

Vegetation growing on soils with high concentrations of trace elements has a tendency of absorbing these elements through its root system and transporting them to other parts of the plant, including fruits (Otieno *et al*., 2005; Ojekunle *et al*., 2014). This study has shown that geothermal spring water contaminates the surrounding surface soil with trace elements. Since the plant depends on the soil for its nutrients, there is a high possibility of it absorbing and transmitting these trace elements. Table 4.11 provides a descriptive summary of the trace elements concentrations in the barks and leaves of *Acacia robusta* and *Mangifera indica* at Tshipise, Siloam and Riverside.

Each of the trace elements' concentrations were compared in each of the seasons. With the leaves of *Acacia robusta*, 19 elements from total elements showed higher concentrations in the summer than the winter, and these included: Be, B, Ti, V, Mn, Cu, Zn, As, Se, Rb, Sr, Mo, Sn, Ba, La, Tl, Hg, Bi and U. Whereas Li, Cr, Co, Ni, Cd, Pb and Sb had higher concentrations in winter compared to the summer season. However, Cs and W remained constant in concentrations in both seasons (Figure 4.17).

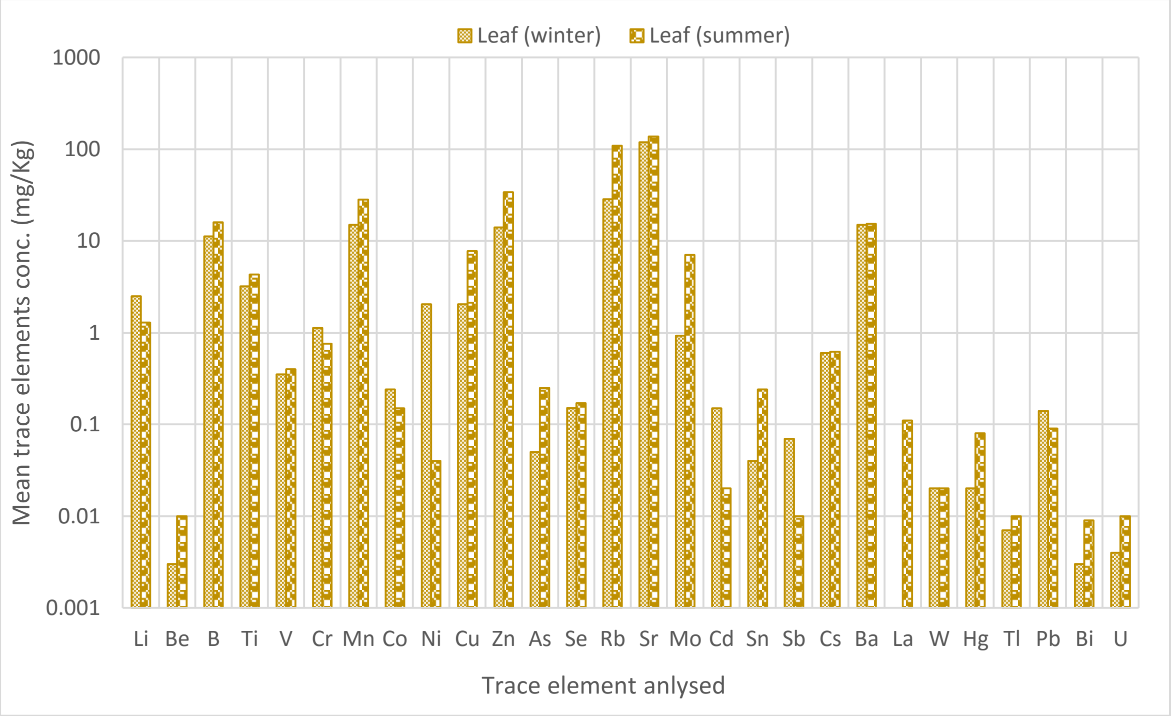


Figure 4.17: Seasonal variation in the trace element concentrations in leaves of *Acacia robusta*

Table 4.11: Descriptive summary of trace element concentrations in *Acacia robusta* and *Mangifera indica* at Tshipise, Siloam and Riverside

	Acacia robusta				Control				Mangifera indica				Control			
	Winter		Summer		Winter		Summer		Winter		Summer		Winter		Summer	
Elements	Bark	Leaf	Bark	Leaf	Bark	Leaf	Bark	Leaf	Bark	Leaf	Bark	Leaf	Bark	Leaf	Bark	Leaf
	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)	(mg/Kg)
Li	0.18	2.50	0.83	1.29	0.93	0.65	1.52	0.62	0.07	0.06	0.59	0.23	0.54	0.99	1.59	3.21
Be	0.01	0.00	0.08	0.01	0.16	0.35	0.18	0.20	0.01	0.00	0.03	0.01	0.01	0.23	0.06	0.56
B	3.40	11.22	6.06	15.92	19.56	9.17	25.14	12.35	2.19	4.75	9.09	12.33	20.02	52.61	25.12	55.24
Ti	11.79	3.20	98.78	4.30	8.80	4.87	32.56	7.89	5.91	2.12	41.57	7.12	63.17	33.12	60.14	59.12
V	2.44	0.35	14.64	0.40	13.94	6.25	23.78	7.01	0.98	0.28	7.31	1.08	4.26	8.50	9.01	17.23
Cr	1.41	1.13	5.10	0.76	9.96	9.82	13.95	5.26	0.87	0.93	2.06	1.14	7.67	8.09	10.28	15.32
Mn	17.00	15.00	307.00	28.22	27.52	14.28	42.16	29.26	27.00	30.00	39.00	1445.00	4.55	32.48	10.12	25.26
Co	0.27	0.24	3.84	0.15	4.76	6.03	6.72	4.83	0.34	0.08	0.48	0.14	3.01	1.41	7.98	3.26
Ni	2.72	2.04	0.04	0.04	2.24	1.36	1.23	0.89	1.78	1.29	0.04	0.04	31.74	33.06	32.10	33.45
Cu	2.47	2.04	22.94	7.73	3.06	2.61	6.86	7.93	2.60	4.09	7.32	128.11	24.04	35.42	32.12	46.12
Zn	10.00	14.00	20.14	33.95	6.57	4.60	10.28	23.12	10.40	10.90	16.22	196.58	24.04	120.73	46.87	129.12
As	0.09	0.05	0.34	0.25	0.31	2.61	0.67	0.54	0.03	0.04	0.37	0.35	0.34	1.65	0.79	2.14
Se	0.13	0.15	0.13	0.17	1.12	3.30	0.89	1.89	0.11	0.11	0.09	0.27	1.22	2.24	5.56	5.01
Rb	1.40	28.40	6.68	108.85	5.50	1.43	15.12	2.34	10.60	4.60	2.16	10.81	33.20	18.68	43.46	39.84
Sr	249.00	119.00	95.95	137.81	25.41	25.04	12.49	13.64	48.00	22.00	563.32	74.80	57.58	39.92	84.01	70.59
Mo	0.18	0.93	0.25	7.05	0.67	1.16	1.24	2.98	0.07	0.17	0.26	0.89	0.81	1.12	1.95	2.84
Cd	0.25	0.15	0.03	0.02	0.55	0.45	0.19	0.14	0.01	0.01	0.02	0.03	0.84	0.02	1.23	0.02
Sn	0.03	0.04	0.26	0.24	0.68	0.86	0.42	0.82	0.01	0.01	0.20	0.90	0.24	0.41	0.68	0.56
Sb	0.02	0.07	0.01	0.01	0.45	0.46	0.03	0.05	0.01	0.01	0.02	0.01	0.13	0.16	0.26	0.32
Cs	0.12	0.60	0.03	0.62	0.22	1.40	0.03	0.76	0.02	0.01	0.00	0.02	0.08	0.07	0.19	0.20
Ba	27.00	15.00	58.39	15.34	25.45	10.27	29.25	11.85	22.00	14.00	57.33	31.50	16.05	28.34	21.58	35.21
La	0.00	0.00	0.57	0.11	0.00	0.00	0.46	0.13	0.00	0.00	0.30	0.11	0.00	0.00	0.01	0.24
W	0.02	0.02	0.02	0.02	0.23	0.52	0.12	0.42	0.01	0.01	0.02	0.14	0.19	0.25	0.34	0.78
Hg	0.01	0.02	0.05	0.08	0.46	1.18	0.01	0.39	0.03	0.03	0.05	0.06	0.26	0.60	1.92	3.10
Tl	0.00	0.01	0.02	0.01	0.43	0.31	0.02	0.01	0.03	0.00	0.01	0.01	0.07	0.05	0.14	1.20
Pb	0.25	0.14	0.05	0.09	1.26	1.54	0.98	1.10	0.14	0.11	0.01	2.94	1.34	1.07	2.31	2.01
Bi	0.01	0.00	0.01	0.01	0.14	0.42	0.01	0.01	0.00	0.00	0.01	0.01	0.07	0.10	0.05	0.12
U	0.10	0.00	0.01	0.01	0.10	0.25	0.10	0.09	0.00	0.00	0.11	0.01	0.07	0.06	0.09	0.08
Count	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00	28.00
Mean	11.80	7.73	22.94	12.98	5.91	4.09	8.33	5.03	4.76	3.42	26.71	70.90	10.93	15.57	14.75	20.33
STDdev	46.90	22.85	61.81	32.60	8.72	5.62	12.09	7.42	10.81	7.30	106.17	278.34	17.67	26.45	21.87	30.60
STD. Error	8.86	4.32	11.68	6.16	1.68	1.08	2.33	1.43	2.04	1.38	20.06	53.57	3.40	5.09	4.21	5.89

In the bark, 67.86% of the elements have higher concentrations in summer than in winter season, which is similar to the leaves. For the bark parts, the elements whose concentrations were higher in summer than winter included: Li, Be, B, Ti, V, Cr, Mn, Co, Cu, Zn, As, Rb, Mo, Sn, Ba, La, Hg, Tl and Bi. In winter, 25% of the elements (Ni, Sr, Cd, Sb, Cs, Pb and U) were present in higher concentrations than in summer, while 7.14% of the elements (Se and W) remained constant in both seasons (Figure 4.18). The higher concentrations in summer for both barks and leaves can be attributed to the rainfall and hot weather which aid the transpiration and evaporation processes from the root system. There is more dissolution of minerals and a higher decomposition rate of organic matter, which are likely to release trace elements into the soil for possible uptake by the surrounding vegetation (McGrath *et al*., 1994). More so, there is fruit formation in the summer, which could also be responsible for the higher concentrations of nutrients, including the trace elements from the soil.

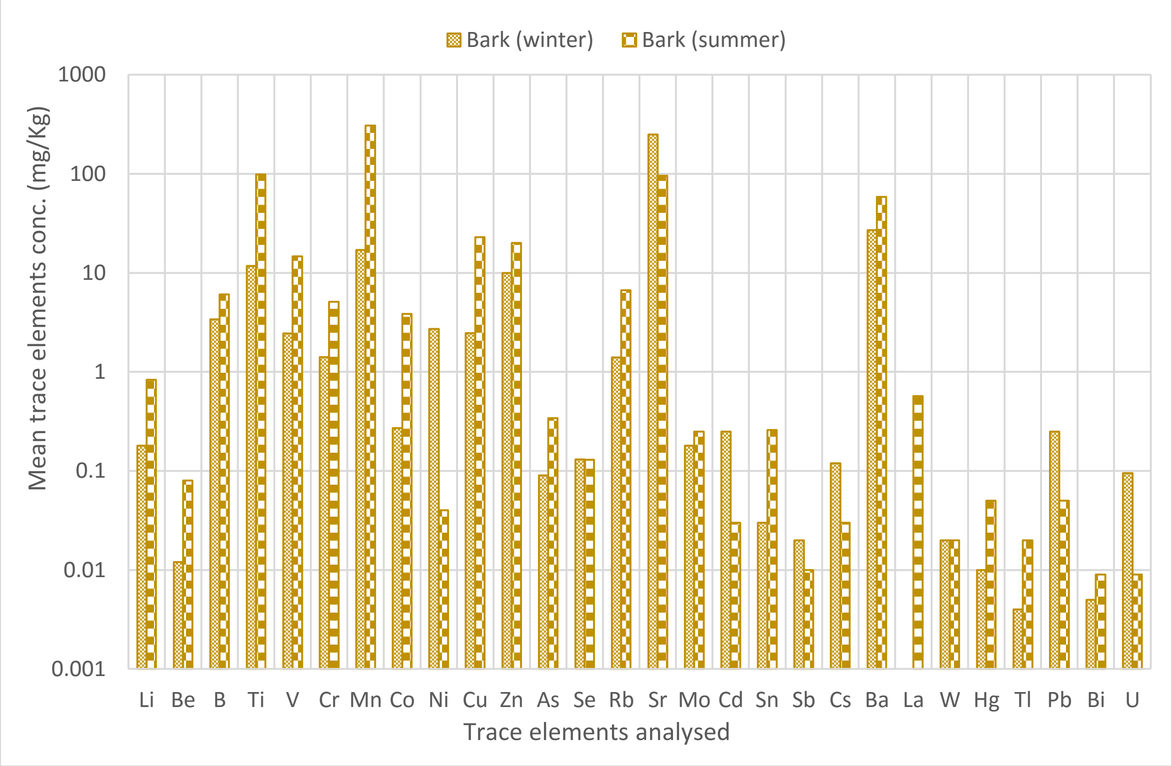


Figure 4.18: Seasonal variation in the trace element concentrations in barks of *Acacia robusta*

At Siloam (*Mangifera indica*) showed a similar behaviour like *Acacia robusta* (Tshipise) with 78.57% of the elements from bark having higher concentrations in the summer compared to the winter season. These elements included Li, Be, B, Ti, V, Cr, Mn, Co, Cu, Zn, As, Sr, Mo, Cd, Sn, Sb, Ba, La, W, Hg, Bi and U. While 21.43% of the elements (Ni, Rb, Cs, Tl, Pb and Se) had higher concentrations in the winter than in summer (Figure 4.19). In the leaves, 92.86% of the elements had higher concentrations in the summer than winter. This implies that there were more elements in the leaves compared to the barks, which shows that there is rapid transpiration process from the root system to the leaves. The elements in the leaves included Li, Be, B, Ti, V, Cr, Mn, Co, Cu, Zn, As, Se, Rb, Sr, Mo, Cs, Cd, Sn, Ba, La, W, Hg, Tl, Pb, Bi and U. There was more Ni concentration in the leaves in winter than in summer and a constant concentration of Sb in both seasons (Figure 4.20). As stated earlier, there is fruit formation during summer, during which the absorbed trace elements will be utilised during the plant's metabolism for fruit formation. Hence, there is more transpiration in the leaf part of *Mangifera indica* from the root system, enriching the leaf parts more, compared to the bark parts (McGrath *et al*., 1994).

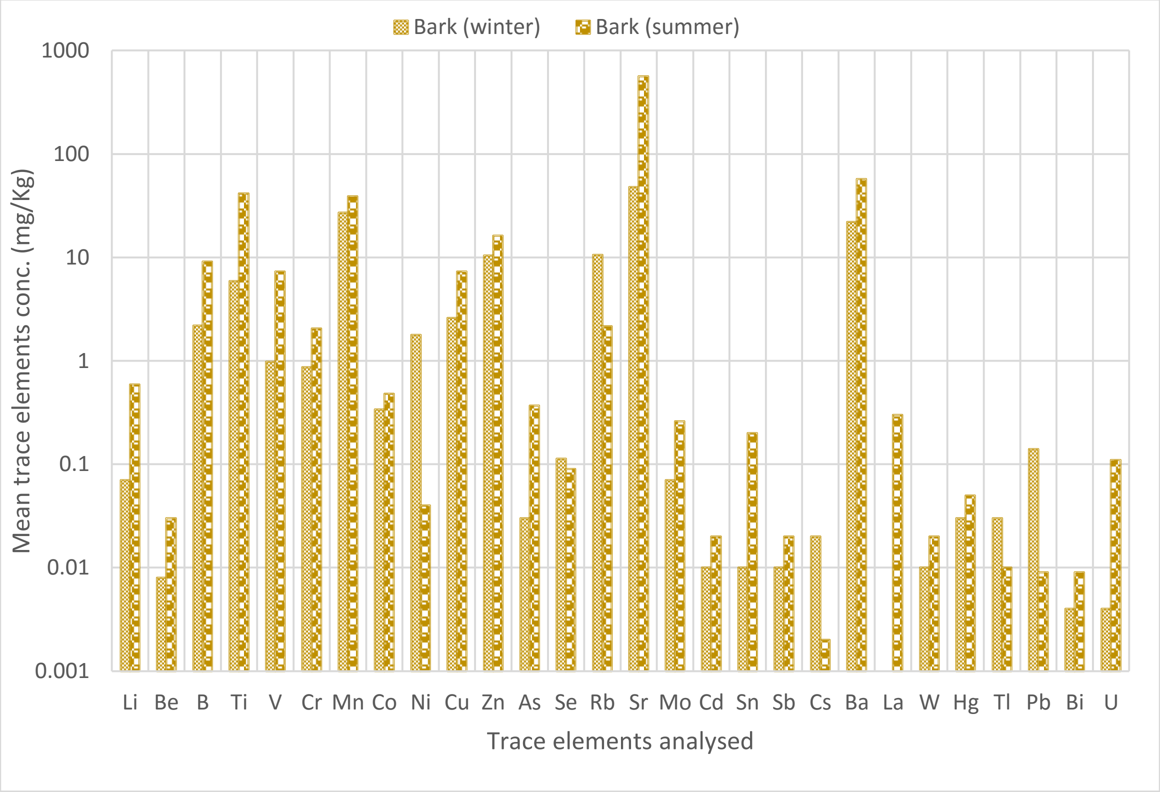


Figure 4.19: Seasonal variation in the trace element concentrations in barks of *Mangifera indica*

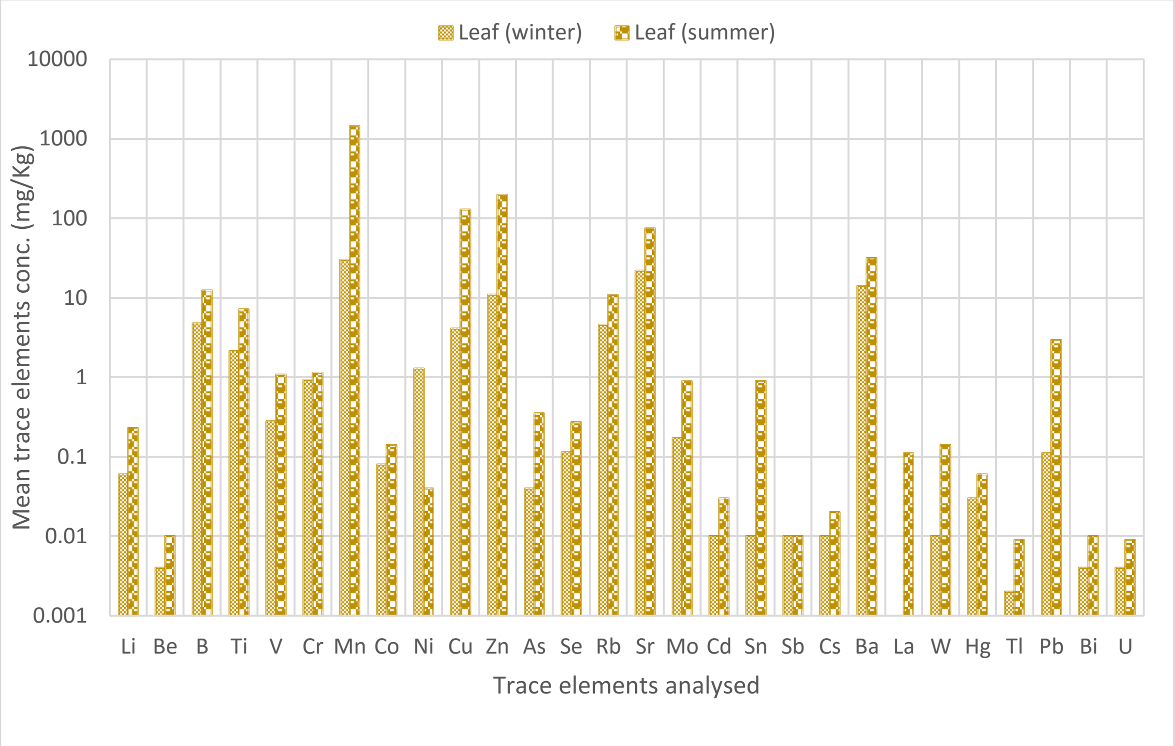


Figure 4.20: Seasonal variation in the trace element concentrations in leaves of *Mangifera indica*

4.4.3 Seasonal variation of trace elements concentrations in *Acacia robusta* and *Mangifera indica*

Statistically, there is a significant difference between the trace elements in the barks and the leaves of *Acacia robusta*. However, there is no statistical significant difference in *Mangifera indica.* Since the p-value is less than 0.05 for *Acacia robusta*, this implies that the differences observed in the trace elements concentrations in the bark and leaves for *Acacia robusta* were real while the differences in concentrations in *Mangifera indica* were by chances, that is, as a result of even distribution of these elements in them. Hence, the differences observed were not statistically significant.

The concentrations of the trace elements in vegetation (*Acacia robusta and Mangifera indica)* have no significant differences ($p > 0.05$) in the columns (the mean difference between each vegetation) (Tables 4.12A and 4.12B) but across the row show that the concentrations of the trace elements differ significantly from bark to leaves of *Acacia robusta* with no significant differences in *Mangifera indica.* The mean concentrations (Table 4.11) show that the barks absorbed more trace elements than leaves in both sites except for *Mangifera indica* in summer when the leaf absorbed more trace elements than the bark. There were more trace elements distribution in summer than in winter season as the control (Figure 4.21).

Table 4.12a: ANOVA for *Acacia robusta* and *Mangifera indica*

A - *Acacia robusta* (leaf and bark)

Source of Variation	SS	df	MS	F	P-value	F critical
Rows	117141.5	27	4338.573	3.984292	**7.56E-07**	1.623786
Columns	3501.859	3	1167.286	1.071968	**0.365712**	2.717343
Error	88202.48	81	1088.92			
Total	208845.8	111				

B - *Mangifera indica* (leaf and bark)

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	668265.6	27	24750.58	1.207888	**0.254771**	1.623786
Columns	77216.15	3	25738.72	1.256112	**0.29503**	2.717343
Error	1659753	81	20490.78			
Total	2405235	111				

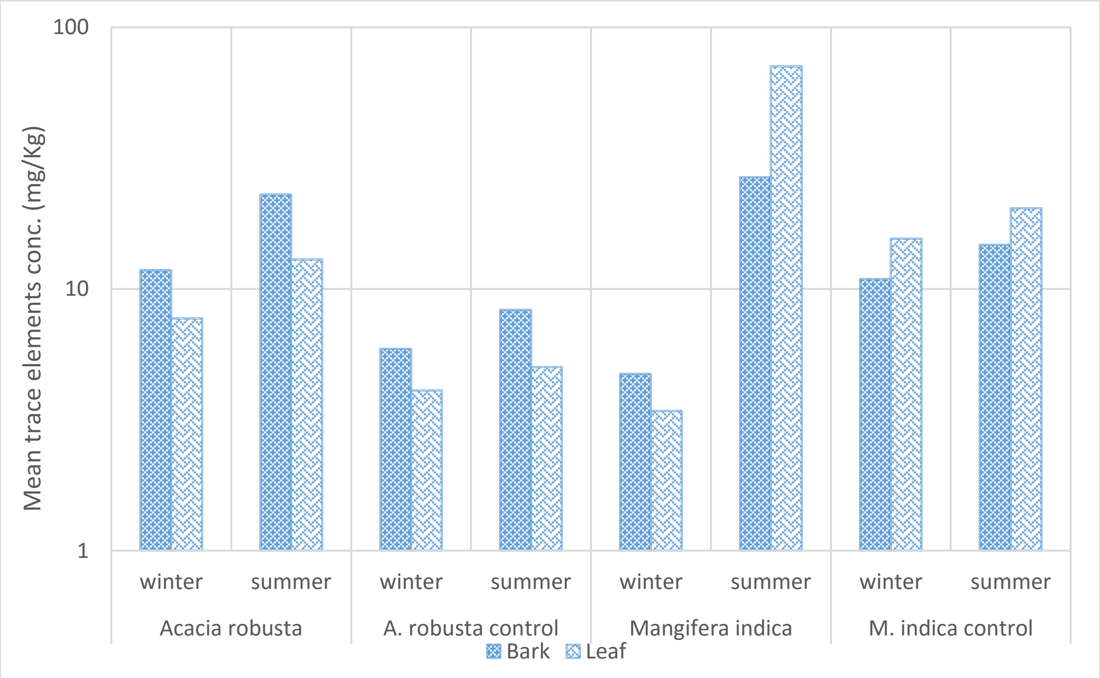


Figure 4.21: Summarised comparison of the mean trace element concentrations of *Acacia robusta*, *Mangifera indica* and their controls

4.4.4 Percentage uptake of the trace elements in *Acacia robusta* and *Mangifera indica*

This study accounts for the uptake of the trace elements in *Mangifera indica* and *Acacia robusta*'s barks and leaves in Siloam and Tshipise. Various plants have been used as bioindicators to assess the impact of pollution sources on the vicinity due to high metal accumulation in plants (Onder and Dursun, 2006). The percentage uptake of the trace elements in the barks and leaves of the plant were calculated using the formula by Lawal *et al.* (2011):

% Conc. of uptake = Conc. of plant's part ÷ (Conc. of plant's part + Conc. of soil) × 100

The percentage mean trace elements uptake by *Mangifera indica* and *Acacia robusta* were (10 – 16) %; (9 -17) % and (13 – 19) %; (39 – 64) % for winter and summer seasons, respectively (Figure 4.22). The determination of the percentage uptake ensured the level of bioaccumulation of these trace elements by each tree. *Acacia robusta* could be used as a bioindicator to access the level of contamination of trace elements in the soil since its uptake capacity is high irrespective of season. However, the study by Ojekunle *et al*. (2014) showed that *Mangifera indica* has a high uptake capability for some selected heavy metals, which this present study cannot justify. This could be as a result of the broader scope from this study considering about 28 trace elements collectively rather than selecting few elements to evaluate their % uptake individually.

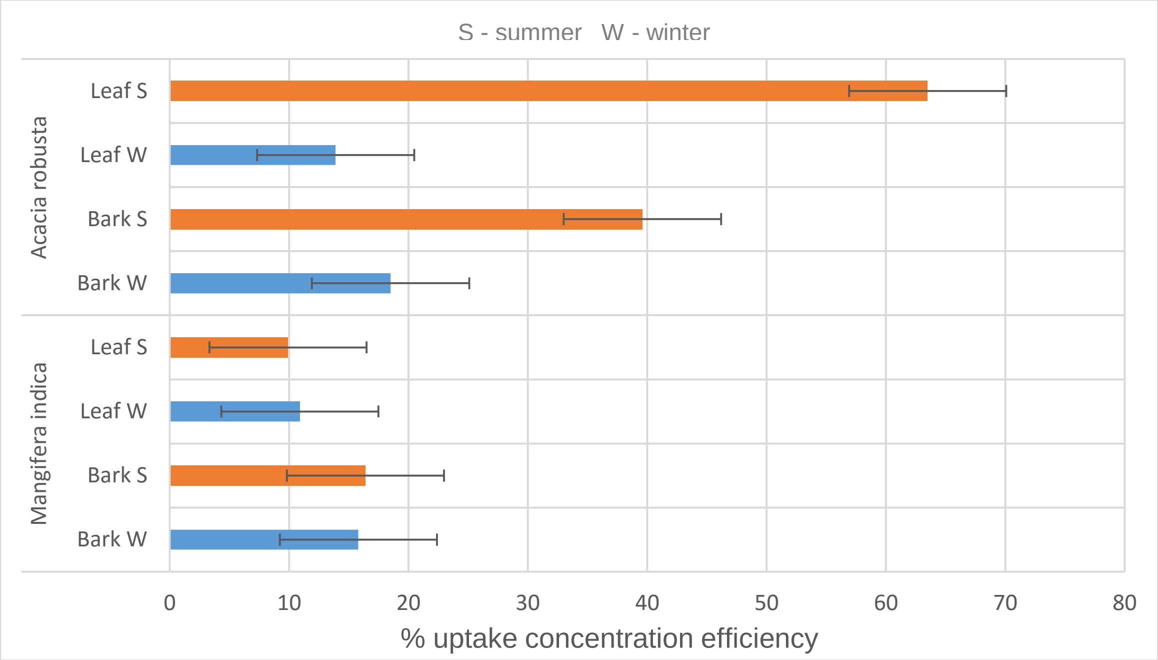


Figure 4.22: Percentage uptake concentrations of the mean trace elements by *Acacia robusta* and *Mangifera indica*

It is difficult to make a conclusive comparison based on the percentage uptake from the two plants because they are growing in different soils with different levels of contamination. As established earlier, the Siloam soils are more contaminated than Tshipise soils, but *Acacia robusta* has been shown to be more efficient in the uptake of trace elements (particularly during summer season). Nevertheless, we can deduce that for economic importance and uptake or phytoremediation, it would be better to plant *Acacia robusta* with a steady rate of uptake than *Mangifera indica* in order to reduce the toxicity of these trace elements.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Preamble

This chapter summarises the outputs of the study on the impacts of trace elements concentrations from the geothermal springs to the neighbouring soil and vegetation. It presents the potential of the geothermal springs to enrich the soil and vegetation with toxic trace elements, which could possibly lead to contamination. The general aim of this study was to investigate the trace element concentrations from the geothermal springs and their impacts on neighbouring soil and vegetation as well as seasonal variations at Siloam and Tshipise springs. In addition, the study incorporated the non-geothermal water, neighbouring soil and vegetation as a control to validate its findings.

5.2 Conclusion

The results from these findings show that the majority of the parameters analysed in the geothermal springs (Siloam and Tshipise) area are reflection of the underlying geology in which the spring originates. In Siloam and Tshipise, some analysed parameters such as fluoride, nickel and lead have higher concentrations compared to the water quality standards. Meanwhile the pH-value at Siloam and mercury level in Tshipise were high. From the neighbouring soil and vegetation samples were analysed to quantify the impacts of the geothermal springs.

From the piper diagrams, the chemical composition of the geothermal water at Siloam is Na-Cl for both seasons; Na-Cl to Ca-Cl_2 in soil for winter and summer; Ca-Cl_2 to Na-Cl in *Mangifera indica* (bark and leaves) for both season. Tshipise geothermal water has chemical composition of $NaHCO_3$ to Ca-$NaHCO_3$ for winter and summer; Na-Cl to Ca-Cl_2 in soil for winter and summer; Ca-Cl_2 and Na-Cl cumulatively in *Acacia robusta* (bark and leaves) for winter and summer season. With respect to the compositional structures from the geothermal spring water, soil and vegetation, it can therefore be deduced that geothermal springs have great influences on the compositions of their neighbouring soils and vegetation.

Factor analyses on trace elements concentrations in the soil samples from both sites also predicted two possible factors. The first factor is attributed to the geothermal water (rock-water interaction at the deep aquifer reflecting the geology of the springs) while the second factor can be attributed to the parent soil formation; that is, soil pedogenesis. Trace elements concentrations from the geothermal springs (Siloam and Tshipise) enrich their surface soils to the point of contamination, leading to the neighbouring vegetation absorbing these trace elements from the soil via transpiration. The mean trace elements concentrations decrease with the indicators (soil pH, SWR, SOM) as we move further away from the geothermal spring. This implies that there is strong correlation between the trace elements concentrations and indicators. This also predicts the impacts of the trace elements (horizontal) status in the surface soil as well as the contamination level.

However, no matter how low the level of trace elements in the environment are, their presence is not desirable because of bioaccumulation. The challenge is to determine the minimum amount of each source of contamination that will result in the accumulation of these trace elements in soils beyond acceptable limits. High levels of Cr, Co, Ni, Cu, Zn and Pb in the soil samples may be linked largely to the geothermal water as well as the parent materials of the soil at Siloam, thereby, making their absorption by vegetation (*Mangifera indica*) inevitable. The soils at Tshipise are moderately concentrated with trace elements, which can be attributed to the moderate concentrations of the trace elements in the geothermal spring water.

Seasonal variation was observed in the parameters analysed in the geothermal spring water, neighbouring soil and vegetation to ascertain the most favourable season in terms of the trace elements availability in the ecosystem. Trace elements concentrations in the geothermal springs were higher during summer than winter; this led to more contamination of their soils and vegetation during summer. Siloam spring water is more mineralised than the Tshipise spring water, hence there are high levels of trace elements in the water, soil and vegetation at Siloam.

This study has shown that the geothermal spring has great potential to enrich the soil and vegetation with trace elements, which could result in contamination. It can thus be concluded that a geothermal spring; despite its benefits to humans also contaminates the soil with toxic trace elements. Soil is the platform for vegetation growth and when the soil is contaminated, there is high possibility that the neighbouring vegetation will absorb these toxic elements which, in-turn, will affect human beings adversely.

5.3 Recommendation

Proper education should be given to the communities at Siloam and Tshipise to caution on the usage of geothermal spring water for domestic and agricultural uses. However, it is further recommended that proper care should be taken with exposure and utilisation of the geothermal spring water at Siloam and Tshipise. Long-term ingestion of this water could possibly pose a great health risk for the consumers because some of the parameters analysed exceeded the South African water quality standards. Among the parameters of concern are fluoride, nickel, lead and mercury levels. It is therefore recommended that the geothermal spring waters at Siloam and Tshipise are monitored on a regular basis, particularly their utilisation. The planting of *Acacia robusta* is more advantageous since its uptake ability is higher than *Mangifera indica.*

Further studies are needed in order to assess more accurately the impacts of these trace elements' intake by plants and animals around the localities.

REFERENCES

Adamu, C.I., Nganje, T.N., Ukwang, E.E., Ibe, K.A. and Peter, N. (2011). A study of the distribution pattern of heavy metals in surface soil around Arufu Pb-Zn mine, Northeastern Nigeria, using factor analysis, *Res. J. Chem. Sci*., vol. 1(2), pp. 70-80.

Adriano, D.C. (1986). Trace elements in the terrestrial environment. Springer-Verlag, New York.

Adriano, D.C. (2001). Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metals, 2nd edn., pp. 860. Springer, New York.

Adriano, D.C., Woodford, T.A., Ciravolo, T.G. (1978). Growth and elemental composition of corn and bean seedlings as influenced by soil application of coal ash. *J .Environ. Qual*., vol. 7, pp. 416-421.

Agarwal, K., Sharma, A. and Talukder, G. (1990). Clastogenic effects of copper sulphate on the bone marrow chromosomes of mice in vivo. *Mutation Research*, vol. 243, pp. 1–6.

Alloway, B.J. (1995). Introduction. In B.J. Alloway (Ed.). Heavy metals in soils. Blackie Academic & Professional, London. pp. 3-10.

Alloway, B.J. and Ayres, D.C. (1997). Chemical Principles of Environmental Pollution. Second Edition, Chapman and Hall, London, pp.140-167.

Alt, F., Eschnauer, H.R., Mergler, B., Messerschmidt, J. and Tolg, G. (1997). A contribution to the ecology and enology of platinum, *Fresenius J Anal Chem*., vol. 257, pp. 1013-1019.

APEC (2010). Drinking water contaminants: Mercury.
Free Drinking Water (http://www.freedrinkingwater.com) accessed November 12, 2013.

Appel, C. and Ma, L. (2001). Concentration, pH and surface charge effect on cadmium and lead sorption in three tropical soils. *J. Environ. Qual*., vol. 31, pp. 581–589.

Baradacs, E., Hunyadi, I., Dezso, Z., Csige, I. and Szerbin, P. (2001). ^{226}Ra in geothermal and bottled mineral waters of Hungary. *Radiation Measurement,* vol. 34, pp. 385-390.

Barton, J.M. (1979). The chemical compositions, Rb-Sr isotopic systematics and tectonic setting of certain post-kinematic mafic igneous rocks, Limpopo Mobile Belt, Southern Africa, *Precambrian Res*., vol. 9, pp.57 – 80.

Basta, N.T., Ryan, J.A. and Chaney, R.L. (2005). Trace element chemistry in residual - treated soil: Key concepts in metal bioavailability. *J. Environ. Qual*., vol. 34, pp. 49-63

Bataillard, P., Cambier, P. and Picot, C. (2003). Short-term transformations of lead and cadmium compounds in soil after contamination. *Eur. J. Soil Sci*., vol. 54, pp. 365–376.

Bertoni, M., Oliveri, F., Manghetti, M., Boccolini, E., Bellomini, M.G., Blandizzi, C., Bonino, F. and del Tacca, M. (2002). Effects of a bicarbonate-alkaline mineral water on gastric functions and functional dyspepsia: a preclinical and clinical study. *Pharmacology Research*, vol. 46, pp.525–531.

Boekhold, A.E., Temminghoff, E.J.M. and Vanderzee, S.E.A (1993). Influence of electrolyte composition and pH on cadmium sorption by an acid sandy soil. *J. Soil. Sci.,* vol. 44, pp. 85–96.

Boekstein, M. (1998). Hot spring holidays: Visitor's guide to hot springs and mineral spa resorts in southern Africa, Cape Town: Mark Boekstein.

Bond, G.W. (1946). A geochemical survey of the underground water supplies of the Union of South Africa*. Memoirs Geol. Surv. S. Afr.,* vol. 41, pp. 208.

Bonfante, L., Calo, L., D'Angelo, A., Favaro, S., Abaterusso, C., Mennella, G., Normanno, M., Spinello, M. and Antonello, A. (1999). Water and its effects when drunk cold. The physician's view. *American Journal of Nephrology,* vol.19, pp.182–184.

Booyens, B. (1981). Bronwaters van genesing - Die tradisionele waterkuur in ons volksgeneeskunde. Kaapstad: Tafelberg.

Bortolotti, M., Turba, E., Mari, C., Lopilato, S., Scalabrino, A. and Miglioli, M. (1999). Effect of a mineral water on gastric emptying of patients with idiopathic dyspepsia. *Int. J. Clinical Pharmacological Research,* vol. 19, pp. 53–56.

Brandl, G. (1986). The geology of the Pietersburg area. Explanation sheet, geological survey of South Africa. vol. 2328 (Pietersburg), pp. 43.

Brandl, G. (2002). The geology of the Alldays area. Explanation sheet geological Survey South Africa. 2228 (Alldays), pp. 71.

Brigatti, M.F., Colonna, S., Malferrari, D., Medici, L. and Poppil, L. (2004). Mercury adsorption by montmotillonite and vermiculite: A combined XRD, TG-MS, and EXAFS study. *Appl. Clay Sci.,* vol. 28, pp. 1–8.

Brock, T.D. (1994). Life at High Temperatures. Yellowstone Association for Natural Science, History, & Education, Inc. Yellowstone National Park, Wyoming, pp. 32.

Brooks, R.R. (1972). Geobotany and biogeochemistry in mineral exploration. Harper and Row, New York, NY, pp. 290.

Bruvold, W.H. and Ongerth, H.J. (1969). Taste Quality of Mineralized Water. *Journal of the American Water works Association*, vol. 61, pp. 170.

Bundt, M., Widmer, F., Pesaro, M., Zeyer, J. and Blaser, P. (2001). Preferential flow paths: Biological 'hot spots' in soils. *Soil Biol. Biochem*., vol. 33, pp. 729–738.

Burt, R., Wilson, M.A., Mays, M.D and Lee, C.W (2003). Major and trace elements of selected pedons in the USA. *J. Environ. Qual.,* vol.32, pp. 2109-2121.

Burk, R., Weber, T., Park, S., Yochum, S. and Fergusson, R. (2011). Trace element concebtration and speciation in selected mining-contaminated soil and water in Willow Creek Floodplain, Colorado, *Applied and Environmental soil science*, 2011, pp. 1-20 .

Buyks, S.E.J., Van de Hoop, M.A.G.T. and Loch, J.P.G. (2002). Dissolution kinetics of heavy metals in Dutch carbonate and sulfide-rich freshwater sediments. *J. Environ. Qual.,* vol. 31, pp. 573–580.

Cakmak, I., Yazici, A., Tutus, Y. and Ozturk, L. (2009). Glyphosate reduced seed and leaf concentrations of calcium, manganese, magnesium, and iron in non-glyphosate resistant soybean. *Eur. J. Agron*., vol. 31, pp. 114–119.

Cantalamessa, F. and Nasuti, C. (2003). Hypocholesterolemic activity of calcic and magnesicsulphate-sulphurous spring mineral water in the rat, *Nutrition Research*, vol. 23, pp. 775–789.

Capurso, A., Solfrizzi, V., Panza, F., Mastroianni, F., Torres, F., Del Parigi, A., Colacicco, A.M., Capurso, C., Nicoletti, G., Veneziani, B., Cellamare, S. and Scalabrino, A. (1999). Increased bile acid excretion and reduction of serum cholesterol after crenotherapy with salt-rich mineral water. *Ageing*, vol. 11, pp. 273–276.

Cassidy, D.P., Werkema, D.D., Atekwana, E.A., Sauck, W.A., Rossbach, S. and Duris, J. (2001). The effects of LNAPL biodegradation products on electrical conductivity measurements. *Journ. Enviro Eng Geo*, vol. 6 (1), pp. 47-52.

Cattlet, K.M., Heil, D.M., Linday, W.L. and Ebinger, M.H. (2002). Soil chemical properties controlling Zn^{2+} activity in 18 Colorado soils. *Soil Sci. Soc. Am. J.,* vol. 66, pp. 1182–1189.

Chen, M., Ma, L.Q and Harris, W.G. (1999). Baseline concentrations of 15 trace elements in Florida Surface soils. *J. Environ. Qual.,* vol. 28, pp. 1173-1181.

Cheney, E. S., Barton, J. M. and Brandl, G. (1990): Extent and age of the Soutpansberg sequences of Southern Africa. *S. Afri. J. Geo.* vol. 93, pp. 644-675.

Chrotowski, P., Durda, J.L. and Edelman, K.G. (1991). The uses of natural processes for the control of chromium migration. *Remediation*, pp. 341-351.

Churchill, R.K. and Clinkenbeard, J.P. (2005). Perspectives on mercury contributions to watersheds from historic mercury mines and non-mine mercury sources: examples from the sulphur creek mining district. Cordilleran Section – 101st Annual Meeting. Piedmont, Italy, 29 April – 1 May 2005.

Cohen, D.R., Shen, X.C., Dunlop, A.C. and Rutherford, N.F. (1989). A comparison of selective soil geochemistry and biogeochemistry in the Cobar area, New South Wales. *Journal of Geochemical Exploration,* vol. 98, pp. 173-189.

Craun, G.F., Calderon, R.L. and Craun, M.E. (2005). Outbreaks associated with recreational water in the United States. *International Journal of Environmental Health Research,* vol. 15 (4), pp. 243-262.

Davies, B.E. (1992). Trace metals in the environment: Retrospect and prospect. In D.C. Adriano (ed.) Biogeochemistry of trace metals. Lewis Publishers, Boca Raton, FL., pp. 1-18.

Davis, J.M. (1999). Oriented carbonate concretions in a paleoaquifer: Insights into geologic controls on fluid flow: *Water Resources Research*, vol. 35, pp. 1705-1712.

De Haan, F.A.M. (1993). Soil quality in relation to soil pollution, In Environmental change and human health (eds. J.V. Lake, F. Willey, G.R. Bock and L. Ackrili) Willey, Chichester, 104 –123

Department of Water Affairs and Forestry (DWAF) (1996). *South African Water Quality Guidelines, Vol. 1: Domestic Water Use* (2nd edn.). Department of Water Affairs and Forestry, Pretoria.

Department of Water Affairs and Forestry (DWAF) (2001). Luvuvhu/Letaba Water Management Area: Water resource situation assessment report NO P0200/00/030/. WSM (pty) Ltd

Department of National Health and Population Development (DNHPD) (1991). Guide: Permissible utilisation and disposal of sewage sludge. Ref: A11/2/5/4, Pretoria.

Dudka, S. and Markert B. (1992). Baseline concentrations of As, Ba, Be, Li, Nb, Sr and V in surface soils of Poland. *Sci. Total Evniron.,* vol. 122, pp. 279-290.

Dunn, C.E., Brooks, R.R., Edmondson, J., Leblanc M and Reeves, R.D. (1996). Biogeochemical studies of metal-tolerant plants from Morocco. *Journal of Geochemical Exploration*, vol. 56, pp. 13-22.

Durowoju, O., Odiyo, J. and Ekosse, G. (2015). Hydrogeochemical setting of geothermal springs in Limpopo Province, South Africa, *Res. J. Chem. Environ*., vol. 19(1), pp. 77-88.

European Union (EU), (1998). Council Directive 98/83/EEC of 3 November 1998 on the quality intended for human consumption, *Official journal of the European Communities*, L330 (5.12.98), pp. 32-53.

European Commission (EC), (1999). Blue Book on Geothermal Resources: A Strategic Plan for the Development of European Geothermal Sector, Alterner: Luxembourg.

Fioravanti, A., Valenti, M., Altobelli, E., Di Orio, F., Nappi, G., Crisanti, A. and Cantarini, L. (2003). Clinical efficacy and cost-effectiveness evidence of spa therapy in osteoarthritis. The results of Naiade Italiana Project, *Panminerva Medica,* vol. 45, pp. 211–217.

Fraioli, A., De Angelis Curtis, S., Ricciuti, G., Serio, A., and D'Ascenzo, G. (2001). Effect of water of Anticolana Valley on urinary sediment of renal stone formers, *Clinica Terapeutica,* vol. 152, pp. 347–351.

Fuller, D.Q. (2009). Advances in Archaeobotanical method and theory: Charting trajectories to domestication, lost crops, and the organization of agricultural labour, In *New Approaches to Prehistoric Agriculture,* pp. 14-59.

Gartley, K. (2011). Recommended Soluble Salts Test., In The North Coordinating Committee for Soil Testing, Recommended Soil Testing Procedures for the Northeastern United States. Northeastern Regional Publication, 493, 3rd (edn).

Garzon, P. and Eisenberg, M.J. (1998). Variation in the mineral content of commercially available bottled waters: implications for health and disease. *American Journal of Medicine,* vol. 105, pp.125–130.

Gasbarrini, G., Candelli, M., Graziosetto, R.G., Coccheri, S. and Di Iorio, F. (2006). Evaluation of thermal water in patients with functional dyspepsia and irritable bowel syndrome accompanying constipation. *World Journal of Gastroenterology*, vol. 12, pp. 2556–2562.

Geo-Heat Center (2005). What is Geothermal? Oregon Institute of Technology, Klamath Falls, (http://geoheat.oit.edu/whatgeo.htm) accessed November 10, 2014.

George, M. (2003). Selenium and Tellurium. Minerals yearbook, Bureau of Mines, U.S., U.S Government printing office, Washington D.C.

Gevers, T.W. (1963). Thermal Springs at Lilani, Natal, and their geologic setting. *Transactions of the Geological Society of South Africa*, vol. LXVI, pp. 129-157.

Grasby, S.E and Leptzik, D.A (2002). Physical properties of Sulphur Mountain thermal springs, Banff National Park, and implications for endangered snails. *Journal of Earth Science,* vol. 39(9), pp. 1349-1361.

Grassi, M., Lucchetta, M.C., Grossi, F. and Raffa, S. (2002). Possibilities of thermal medicine in gastrointestinal functional disorders, *Clinica Terapeutica,* vol. 153, pp.195–206.

Gray, N.F. (2008). Drinking water quality (2nd edn). Cambridge University press, New York, pp. 191-200, ISBN- 978-0-521-87825-8.

Harter, R.D. and Naidu, R. (2001). An assessment of environmental and solution parameter impact on trace-metal sorption by soils. *Soil Sci. Soc. Am. J.,* vol. 65, pp. 597–612.

Hartnady, C.J.H. and Jones, M.Q.W (2007). Geothermal Studies of the Table Mountain Group Aquifer Systems, Water Research Commission, Report No. 1403/1/07.

Harvey, D. (2000). Modern analytical chemistry. International edition. Mc Graw-Hill Company. ISBN: 0-07-116953-9

Hayashi, H. (2008). The scientific benefits of drinking alkaline ionised water, Alkaline Water Health, (http://www.AlkalineWaterHeath.com) accessed February 18, 2014.

Helfrich, L.A, Parkhurst, J and Neves, R. (2005). Managing spring wetlands for fish and wildlife habitat. *Virginia Cooperative Extension*, vol. 420 (537), pp. 1-6.

Hellman, M.J and Ramsey, M.S. (2004). Analysis of hotsprings and associated deposits in Yellowstone national park using ASTER and AVIRIS remote sensing. *Journal of volcanology and geothermal research,* vol. 135, pp.195 – 219.

Higgins, M.D and Higgins, R. (1996). A Geological Companion to Greece and the Aegean, Gerald Duckworth: London, United Kingdom.

Hodder, A.P.W. (2005). Geothermal waters: a source of energy and metals, Department of Earth Sciences, University of Waikato) XIII-Water-AGeothermal-10, (http://nzic.org.nz/ChemProcesses/water/13A.pdf) accessed in December 12, 2014.

Hoffmann, E.L. (1989). Instrumental neutron activation analysis as an analytical technique for gold exploration. *Journal of Geochemical Exploration,* vol. 32, pp. 301-308.

Hoole, R. J. (2001). The Development of Lilani Hot Springs: An Analysis of socio-economic and environmental impacts, Dissertation submitted in fulfilment of the degree of Masters of Science in the Department of Geography, University of Natal: Pietermaritzburg.

Huang, P.M., Violante, A., Bollag, J.M. and Vityakon, P. (2005). Soil abiotic and biotic interactions and impact on the terrestrial ecosystem and human welfare. Science Publishers, Plymouth, UK.

Ifegwu, C. and Anyakora, C. (2012). Screen for eight heavy metals in groundwater samples from highly industrialized area of Lagos, Nigeria. *Afri. Journal of pharmaceutical science and pharmacy,* vol. 3(1), pp. 1-16.

Izumiyama, S., Yagita, K., Furushima-Shimogawamasakura, T., Karasundani, T and Endo, T. (2003). Occurrence and distribution of Naegleria species in thermal waters in Japan. *J. Eukaryot Microbiol*., vol. 50 (1), pp. 514.

Jansen, H. (1975). The Soutpansberg trough (northern Transvaal) — an aulacogen. *Transactions of the Geological Society of South Africa,* vol. 78, pp.129–36.

Jarup, L., Berglund, M., Elinder, C.G., Nordberg, G and Vahter, M. (1998). Health Effects of Cadmium Exposure--a Review of the Literature and a Risk Estimate. *Scandinavian Journal of Work, Environment & Health,* vol. 24(1), pp. 1-51.

Johnson, M.R., Anhaeusser, C.R. and Thomas, R.J. (2006). The geology of South Africa. Published jointly by the geological society of South Africa, Johannesburg and the council for geosciences, Pretoria, pp. 301 – 318.

Johnson, R. and Scherer, T. (2009). Drinking water quality: Testing and interpreting your results, North Dakota State University (NDSU), (http://www.ag.ndsu.edu) accessed November 10, 2014.

Kabata-Pendias, A and Pendias, H. (2001) Trace elements in soils and plants. 3rd edn. CRC Press, London.

Karapanagiotis, N.K., Sterritt, R.M. and Lester, J.N. (1991). Heavy metals complexation in sludge amended soil. The role of organic matter in metals retention. *Environ. Technol.,* vol. 12, pp. 1107–1116.

Kempster, P.L., van Vliet, H.R. and Kuhn, A. (1997). The need for guidelines to bridge the gap between ideal drinking water quality and that quality which is practically achievable and acceptable, *Water SA*, vol. 23(2), pp. 163-167.

Kent, L. E. (1942). The Letaba hot spring. *The Transaction of the Royal Society of South Africa,* vol. 29 (2), pp. 35-47

Kent, L.E. (1946). The warm springs at Loubad near Nylstroom. *The Transaction of the Royal Society of South Africa*, vol. 31(2), pp. 151-168.

Kent, L.E. (1949). Thermal waters of the Union of South Africa and South West Africa. *Trans. Geol. Soc. WS. Afr.,* vol. 52, pp. 231-264.

Kent, L.E. (1969). The Thermal Waters in the Republic of South Africa, International Geological Congress, Report of the Twenty-Third session, Czechoslovakia, Proceedings of Symposium II, Mineral and Thermal Waters of the world-Overseas countries, vol. 19, pp. 143-164.

Kent, L.E. and Groeneveld, D. (1962). Warm and Cold Springs on Richmond, Pilgrim's Rest District, Transvaal, *Annals of the Geological Survey of South Africa,* vol. (1), pp. 175-182.

Kevin, T., McCarthy, T.P and Roy, E. (2005). Geochemistry of Champagne Hot Springs shallow hydrothermal vent field and associated sediments, Dominica, Lesser Antilles. *Chemical Geology,* vol. 224, pp. 55–68.

La Moreaux, P.E and Tanner, J.T. (2001). Springs and Bottled Waters of the World, Ancient History, Source, Occurrence, Quality and Use, Springer: Berlin.

Lang, F. and Kaupenjohann, M. (2003). Effect of dissolved organic matter on the precipitation and mobility of the lead compound chloropyromorphite in solution. *Eur. J. Soil Sci.,* vol. 54, pp. 139–147.

Lasat, M.M. (2002). Phytoextraction of toxic metals: A review of biological mechanisms. *J. Environ. Qual.,* vol. 31, pp.109–120.

Lawal, A.O., Batagarawa, S.M., Oyeyinka, O.D. and Lawal, M.O (2011). Estimation of Heavy Metals in Neem Tree Leaves along Katsina – Dutsinma – Funtua, Highway in Katsina State of Nigeria, *J. Appl. Sci. Environmental Management*. June, 2011, vol. 15 (2), pp. 327 – 330.

Leavitt, S.W., Deuser, R.D. and Goodell, H.G. (1979). Plant regulation of essential and non-essential heavy metals. *Journal of Applied Ecology,* vol. 16, pp. 203-212.

Lenntech (1998-2009). Selenium (Se) chemical properties, health and environmental effects, (http://www.lenntech.com/periodic/elements/se.htm) accessed May 25, 2014.

Lipfert, G., Reeve, A.S. Sidle, W. and Marvinney, R. (2004).Geochemical patterns in an arsenic – tainted, fracture – bedrock groundwater system in Northport, Maine USA, Applied Geochemistry (In review).

Liu, C., Lin, K. and Kuo, Y. (2003). Application of factor analysis in the assessment of groundwater quality in a black foot disease area in Taiwan, *The science of the total environment*, vol. 313, pp. 77-89.

Lund, J.W. (2000). Balneological use of thermal water in the USA, GHC Bulletin, September, pp. 31-34.

Lund, J.W. and Freeston, D.H. (2001). World-wide direct uses of geothermal energy 2000. *Geothermics*, vol. 30, pp. 29-68.

Ma, L.Q.Y. (1996). Factors influencing the effectiveness and stability of aqueous lead immobilization by hydroxyapatite. *J. Environ. Qual.,* vol. 25, pp. 1420–1429.

Ma, L.Q., Tan, F and Harris, W.G. (1997). Concentrations and distributions of eleven metals in Florida soils. *J. Environ. Qual*., vol. 26, pp. 769-775.

Magdoff, F.R, Tabatabai, M.A and Hanlon E.D. (1996). Soil Organic Matter: Analysis and Interpretation. Soil Sci. Spec. Pub. No. 46:21-31.

Makungo, T.E. (2008). The adequacy of water supply to meet the demand in Siloam Village of Limpopo Province of South Africa, Honours dissertation, Department of Hydrology Water Resources, University of Venda, South Africa. pp 92.

Makungo, R., Odiyo, J.O., Ndiritu, J.G. and Mwaka, B. (2010). Rainfall–runoff modelling approach for ungauged catchments: A case study of Nzhelele River sub-quaternary catchment.

Malini, S., Nagaiah N., Paramesh L and Wenkatarmiah P. (1995). Study of the distribution of trace elements in soils in and around Mysore city, Karnataka. *Environ. Geol.,* vol. 26, pp. 107-110.

Malla, P. B. (2002). Vermiculites. In ‘‘Soil Mineralogy with Environmental Applications’’ (J. B. Dixon and D. G. Schulze, Eds.). SSSA Chapter 16. Book series, no. 7, WI, pp. 501–529.

Mamba, B., Rietveld, L and Verbeck, J. (2008). SA drinking water standards under the microscope, *The Water Wheel,* vol. 7 (1), pp. 24-27.

Manda, L. and Suzuki, K.T. (2002). Arsenic round the world: a review. *Talanta,* vol. 58 (1), pp. 201-235.

Manning, B.A. and Goldberg, S. (1996). Modelling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. *Soil Sci. Soc. Am. J.,* vol. 60, pp. 121–131.

Maskall, J.E. and Thornton, I. (1998). Chemical partitioning of heavy metals in soils, clays and rocks at historical lead smelting sites. *Water, Air, Soil Pollut.,* vol. 108, pp. 391–409.

McGrath, S.P., Chang, A.C., Page, A.L. and Wilter, E. (1994). Land application of sewage sludge: scientific perspective of heavy metal loading limits in Europe and United States. *Environ. Rev*., vol. 2, pp. 108-118.

Mezhals, G.V. (1996). Trace elements in soils of Latavia. Euras. *Soil Sci*., vol. 28, pp. 123-128.

Miyamoto, H., Jitsurong, S., Shiota, R., Maruta, K., Yoshida, S. and Yabuuchi, E. (1997). Molecular determination of infection source of a sporadic Legionella pneumonia case associated with a hot spring bath. *Microbial. Immunol.,* vol. 41 (3), pp. 197-202.

Mountain Nature, (2003). Hot Springs. MountainNature.com, the Field Guide for the next millennium. (http://www.mountainnature.com/Geolomlgy/HotSprings.ht) Accessed September 24, 2014.

Mundalamo H.R. (2003). Investigation of water quality in Nzhelele valley, Limpopo province, South Africa, honours mini-dissertation (Unpublished), University of Venda, Thohoyandou.

Murray, K.S., Rogers, D.T. and Kaufman, M.M. (2004). Heavy metals in an urban watershed in South-eastern Michigan. *J. Environ. Qual.,* vol. 33, pp. 163–172.

Naidu, R. and Harter, R.D. (1998). Effect of different organic ligands on cadmium sorption by and extractability from soils. *Soil Sci. Soc. Am. J.*, vol. 62, pp. 644–650.

National Health and Medical Research Council (NHMRC) (2004). Australian Drinking Water Guidelines, (http://www.nhmrc.gov.au/publications/synopses/eh19sun.htm) accessed March 30, 2014.

Nelson, K. (2002). Application of the Prescott active management area groundwater flow model, planning scenario 1999 – 2025, Modelling report No. 12, Phoenix, Arizona: Arizona department of water resources, hydrology division.

Nerbrand, C., Agreus, L., Lenner, R.A., Nyberg, P. and Svardsudd, K. (2003). The influence of calcium and magnesium in drinking water and diet on cardiovascular risk factors in individuals living in hard and soft water areas with differences in cardiovascular mortality. *BMC Public Health*, vol. 3, pp. 21.

New Hampshire Department of Environmental Services (2007). Beryllium in drinking water, Environmental Fact Sheet, New Hampshire, (www.des.nh.gov) accessed January 21, 2014.

New Mexico Environment Department, (2002). Use Attainability of Sulphur Creek Sandoval County, New Mexico. Surface Water Quality Bureau, 15 April 2002.

Nguyen, K. (2007). Answers to a nation's prayers. *City Press.* Accessed 7 October 2014.

Nordberg, G.F., Goyer, R.A. and Clarkson, T.W. (1985). Impact of effects of acid precipitation on toxicity of metals. *Environmental Health Perspectives*, vol. 68, pp. 169–180.

NIOSH (2003). Method 7303: Elements by ICP (Hot Block/HCl/HNO_3 Ashing), NIOSH Manual of Analytical Methods, Fourth Edition, Issue 1, March 15, 2003, pp. 1-6.

Ntsoane, O. (2001). A typology of indigenous cultural heritage sites as educational material. A paper presented to the South African Heritage Resource agency and Local Government seminar held in Grahamstown, 15 February 2002.

Odiyo, J.O and Makungo, R. (2012). Fluoride concentrations in groundwater and impact on human health in Siolam Village, Limpopo Province, South Africa, *Water SA*., vol. 38 (5), pp. 731-736.

Olivier, J., Van Niekerk, H.J. and Van Der Walt, I.J. (2008). Physical and Chemical characteristics of thermal springs in the Waterberg area of Limpopo Province, South Africa. *Water SA,* vol. 34 (2), pp. 163-174.

Olivier, J., Venter, J.S. and Jonker, C.Z. (2011). Thermal and Chemical Characteristics of Thermal Springs in the Northern Part of the Limpopo Province, South Africa, *Water SA,* vol. 34 (2), pp. 163-174.

Olivier, J., Venter, J.S. and Van Niekerk., H.J. (2010). Physical and Chemical Characteristics of Thermal Springs in Limpopo Province, South Africa, proceedings of World Geothermal Congress 2010, Bali, Indonesia, pp. 13.

Ojekunle, Z.O., Ubani, D.R and Sangowusi, R.O. (2014). Effectiveness of Neem, Cashew and Mango trees in uptake of heavy metals in mechanic village, Merits Res. *Journ. Envin. Sci. and Tox.,* vol. 2(8), pp. 185 – 190.

Onder, S. and Dursun, S. (2006). Air borne heavy metal pollution of Cedrus libani (A. Rich.) in city center of Konya (Turkey). *Atmospher. Environ.,* vol. 40 (6), pp. 1122-1133.

Otieno, D., Schmidt, M.U.I., Adiku, S.T.K. and Tenhunen, J.D. (2005). Physiological and morphological responses to water stress in two acacia species from contrasting habitats, *Tree Physiology*, vol. 25, pp. 361-371.

Pais, I. and Jones, J.B. (1997). The handbook of trace elements. St. Lucie Press, Boca Raton, FL.

Pankurst, R. (1990). The use of thermal baths in treatment of skin diseases in old time Ethiopia. *International Journal of Dermatology*, vol. 29(6), pp. 451-456.

Petraccia, L., Liberati, G. and Masciullo S.G. (2005). Water, mineral waters and health. *Clinical Nutrition,* vol. 25 (3), pp. 377-385.

Piper, A.M. (1944). A graphic procedure in geochemical interpretation of water analyses. *Trans Am Geophys Union*, vol. 25, pp. 914–923.

Pleysier, L.J. (1995). Soil sampling and sample preparation. IITA Research Guide 2.

Popovski, K and Vasilevska, S.P. (2003). What about further development of geothermal energy use in agriculture? Problems and possibilities, *European Geothermal Conference 2003*, Session: Agricultural direct use, (http://pangea.stanford.edu/ERE/db/IGAstandard/record_detail.php?id=684) accessed July 16, 2014.

Press, F. and Siever, R. (1986). Earth, 4th ed., W.H. Freeman and Company: New York.

Pyle, S.M., Nocerino, J.M., Deming, S.N., Palasota, J.A., Palasota, J.M., Miller, E. L., Hillman, D.C., Kuharic, C.A., Cole, W.H., Fitzpatrick, P.M., Watson, M.A. and Nichols, K.D. (1996). Comparison of AAS, ICP-AES, PSA, and XRF in determining Lead and Cadmium in Soil. *Environ. Sci. and Tech.*, vol. 30, pp. 204-213.

Raju, K.K. and Raju, A.N. (1999). Biogeochemical investigation in south eastern Andhra Pradesh: the distribution of rare earths, thorium and uranium in plants and soils. *Environ. Geo.,* vol. 39, pp. 1102-1106.

Rindl, M. (1936). The Medicinal Springs of South Africa, South African Railways and Harbours: Pretoria.

Robinson, M.S., Anthony, T.R., Littau, S.R., Herckes, P., Nelson, X., Poplin, G.S. and Burgess, J.L. (2008). Occupational PAH exposures during prescribed pile burns. *Ann. Occ. Hyg.,* vol. 52(6), pp. 497–50.

Romero, L., Alomso, H., Campano, P., Fanfani, L., Cidu, R., Dadea, C., Keegan, T., Thornton, I. and Farago, M. (2003). Arsenic enrichment in waters and sediments of the Rio Loa (Second Region, Chile). *Appl. Geochem.,* vol. 18 (9), pp. 1399-1416.

Rybicka, E.H, Calmano, W., and Breeger, A. (1995). Heavy metals sorption/desorption on competing clay minerals and experimental study. *Appl. Clay Sci*., vol. 9, pp. 369–381.

Sajil Kumar, P.J. (2013). Interpretation of groundwater chemistry using Piper and Chadha's diagrams: a comparative study from perambalur taluk, *Elixir Geosciences*, vol. 54, pp. 12208 - 12211

Salocks, C. and Kaley, K.B. (2003). Lithium: Technical Support Document: Toxicology Clandestine Drug Labs: Methamphetamine, *OEHHA,* vol. 1(4), pp. 1-10.

Scancar, J., Milacic, R. and Horvat, M. (2003). Comparison of various digestion and extraction procedures in analysis of heavy metals in sediments. *Water, air and soil pollution*, vol. 118, pp. 87 – 99.

Scheffel, R. L. and Wernett, S.J. (1980). Natural Wonders of the World Readers Digest. The Readers digest association: New York.

Schmitt, D., Taylor, H.E., Aiken, G.R., Roth, D.A. and Frimmel, F.H. (2002). Influence of natural organic matter on the adsorption of metal ions onto clay minerals. *Environ. Sci. Technol.,* vol. 36, pp. 2932–2938.

Schoppen, S., Pérez-Granados, A.M., Carbajal, A., Oubina, P., Sanchez-Muniz, F.J., Gomez-Gerique, J.A. and Vaquero, M.P. (2004). A sodium-rich carbonated mineral water reduces cardiovascular risk in postmenopausal women', *Journal of Nutrition*, vol. 134, pp. 1058–1063.

Serio, A. and Fraioli, A. (1999). An observational and longitudinal study on patients with kidney stones treated with Fiuggi mineral water. *Clinica Terapeutica*, vol. 150, pp. 215–219.

Shi, B. and Sengupta, A. (1995). Leaching behaviour of fly ash piles: the phenomenon of delayed rise in toxic concentrations. *J. Environ. Syst*., vol. 24, pp. 87-93

Siegel, F. R. (2002). Environmental Geochemistry of Potentially Toxic Metals, *Springer-Verlag, Berlin,* 218.

Singh, N. and Yunus, M. (2000). Environmental impacts of fly ash. Ln: Iqbal M, Srivastava PS, Siddiqui TO (eds) Environmental hazards: plant and people. CBS, New Delhi, pp. 60-79.

Skapare, I., Kreslins, A. and Gjunsburgs, B. (2003). Balneological properties of the geothermal water in Latvia, Proceedings of the European Geothermal Conference, Hungary, (http://www.geothermie.de/egec-geothernet/proceedings/szeged/o-6-03) accessed May 7, 2014.

Skoryna, S.C (1981). Effects of oral supplementation with stable strontium, *CMA Journal,* October, vol. 125, pp. 703-712.

Smith, G.T., Goldman, M.S., Greenbaum, P.E. and Christiansen, B.A. (1995). Expectancy for social facilitation for drinking: the divergent paths of high expectancy and low expectancy adolescents. *J. Abnorm. Psycho.,* vol. 104 (1), pp. 32-42.

Smith, M. and Puczko, L. (2009). Health and wellness tourism. Elsevier: Tokyo.

South African Bureau of Standards (SABS) (1999). Class 1 Potable Water Standards. SABS 241:1999. South African Bureau of Standards Pretoria, South Africa.

Spalding, R.F. and Exner, M. E. (1993) Occurrence of nitrate in groundwater—a review: Journal of Environmental Quality, v. 22, p. 392–402.

Spicer, S. and Nepgen, J. (2005). Holistic holidays in South Africa-health spas, hot springs, magical places and sacred spaces*.* Cape Town, Human & Rousseau.

SR ISO 11466 – 1999. Soil quality - Extraction of trace elements soluble in aqua regia. International Organization for Standardization, Geneva, Switzerland.

Sugita, M., Grant, E.P., van Donselaar, E., Hsu, V.W., Rogers, R.A., Peters, P.J. and Brenner, M.B. (1999). Separate pathways for antigen presentation by CD, *molecules. Immunity,* vol. 11, pp. 743–752.

Tack, F.M.G., Verloo, M.G., Vanmechelen, L. and Van Ranst, E. (1997). Baseline concentration levels of trace elements as a function of clay and organic carbon contents in soils in Flanders (Belgium). *Science of the Total Environment,* vol. 201, pp. 113-123.

Tamura, T. (1972). Sorption phenomena significant in radioactive waste disposal. In ‘‘Underground waste management and environmental implications’’ (T. D. Cook, Ed.). Proc. of Symp., Houston, TX. Memoir no 18. *Am. Assoc. Petrol. Geol*., pp. 318–330.

Taylor, J. and Phillips, F. (2007). Balneology or taking waters. (www.selfgrowth.com) accessed October 21, 2014.

Taylor, M.D. and Theng, E.K.G. (1995). Sorption of cadmium by complexes of kaolinite with humic acid, *Commun Soil Sci. Plant Anal*., vol. 26, pp. 765–776.

Tekere, M., Adele, L., Olivier, J., Jonker, N., and Venter, F. (2012). Metagenomic analysis of bacterial diversity of Siloam hot water spring, Limpopo, South Africa. *Afri. J. Biotechnol*., vol. 10, pp. 18005-18012.

Temminghoff, E.J.M., van Der Zee, S.E.A. and De Haan, F.A.M. (1998). Effects of dissolved organic matter on the mobility of copper in a contaminated sandy soil. *Eur. J. Soil Sci.*, vol. 49, pp. 617–628.

Tiller, K.G., Gerth, J. and Brummer, G. (1984). The relative affinities of Cd, Ni and Zn for different soil clay fractions and goethite. *Geoderma,* vol. 34, pp. 17–35.

Todd, D.K. (1980). Groundwater Hydrology, 2nd edition. xiii + 535 pp., numerous figs and tables. New York, Chichester, Brisbane, Toronto: John Wiley. ISBN 0 471 87616X

Toussaint, C., Peuchant, E., Nguyen, B.C., Jensen, R. and Canellas, J. (1986). Influence of calcic and magnesic sulphurous thermal water on the metabolism of lipoproteins in the rat, *Archives Internationales de Physiologie de Biochimie et de Biophysique*, vol. 94, pp.65–76.

Tree Fruit research & Extension center, (2004). Chemical properties of soil, Washington state University, 1100 N Western Ave., Wenatchee, WA, 98801 USA

Tshibalo, A.E. (2011). Strategy for the sustainable development of thermal springs: A case study for Sagole in Limpopo province .Unpublished PhD. Thesis, University of South Africa.

Tyler, G. and Olsson, T. (2001). Concentration of 60 elements in the soil solution as related to the soil acidity. *Eur. J. Soil Sci*., vol. 52, pp. 151–165.

United State Environmental Protection Agency (USEPA) (1993). Clean Water Act. Standards for the use and disposal of sewage sludge. Code of Federal Regulations (CFR) Part 503, vol. 58, No. 32. U.S. Environmental Protection Agency, Washington, DC.

United State Environmental Protection Agency (USEPA) (2004). Guideline for Water Reuse. EPA, Washington DC, EPA/625/R-04/108.

United State Environmental Protection Agency (USEPA) (2009). 2009 Edition of the Drinking Water Standards and Health Advisories, EPA: Washington DC.

Usuda, K., Kono, K., Dote, T., Watanabe, M., Shimizu, H., Tanimoto, Y. and Yamadori, E. (2007) An overview of boron, lithium and strontium in human health and profiles of these elements in urine of Japanese, *Environmental Health and Preventative Medicine,* vol. 12, pp. 231-237.

Vangheluwe, M., Van Sprang, P., Verdonck, F., Heijerick, D., Versonnen, B., Vandenbroele, M., and Van Hyfte, A. (2005). Metals Environmental Risk Assessment Guidance. UK Government – Department for Environment Food and Rural Affairs (Defra)

Van Eeden, O. R., Visser, H.N., Van Zyl, J. S., Coertze, F. J. and Wessel, J. T. (1955). The geology of the eastern Soutpansberg and the Lowveld to the north. Explanation Sheet 42 (Soutpansberg), geological Survey of South Africa, 117.

Van Vuuren, K. (1990). Die Warmwaterbronne van Suidwes-Kaapland: HulleVerbreiding, Eienskappe en Benutting. B.A. Honours dissertation, University of Stellenbosch.

Vimmerstedt, L.T. (1998). Opportunities for small geothermal projects: Rural power for Latin America, the Carribbean and the Philippines. Natural renewable energy laboratory, Colorado, USA.

Virk, H.S., Sharma, A.K and Kurma, N. (1998). Radon/Helium survey of thermal springs of Parbati, Beas, Sutlej Valleys in Himachal. *Journal of the Geological Society of India, vol.* 52(5), pp. 523-528.

Visser, D.J.L (1989). The Geology of the Republics of South Africa, Transkei, Bophuthatswana, Venda and Ciskei and the Kingdom of Lesotho and Swaziland, 4th ed., Department of Mineral and Energy Affairs, Pretoria, South Africa.

Wang S. and Xie G. (2003). Geothermal water for multiple purposes in Beijing, Beijing Institute of Geological Engineering and Exploration, China.

Water UK (2001).Cadmium briefing paper, Water UK: London.

Watson, K. (1997). Geyser, Fumaroles and Hot Springs. USGS. 31 Jan. 1997 (7 Jun. 2003).

Wild, A. (ed) (1988). Russell's Soil Conditions and Plant Growth, 11th edn., Longman Scientific & Technical, Harlow, Essex, UK.

Witcher, J.C. (1981). Thermal springs of Arizona. *Earth Sciences and Mineral Resources in Arizona,* vol. 11(2), pp. 1-4.

Witcher, J.C. (2002). Masson Radium Springs Farm. Southwest Technology Institute, New Mexico State University.

World Health Organisation (WHO) (2000). Bottled drinking water, (http://www.who.int/mediacentre/factsheets/fs256/en/print.html) accessed August 19, 2014.

World Health Organisation (WHO) (2003). Selenium in drinking water, Background document for development of WHO Guidelines for Drinking-water Quality, WHO: Geneva.

World Health Organisation (WHO) (2008). Guideline for Drinking-water Quality, 3rd ed., Incorporating the First and Second Addenda, Volume 1, Recommendations, WHO: Geneva.

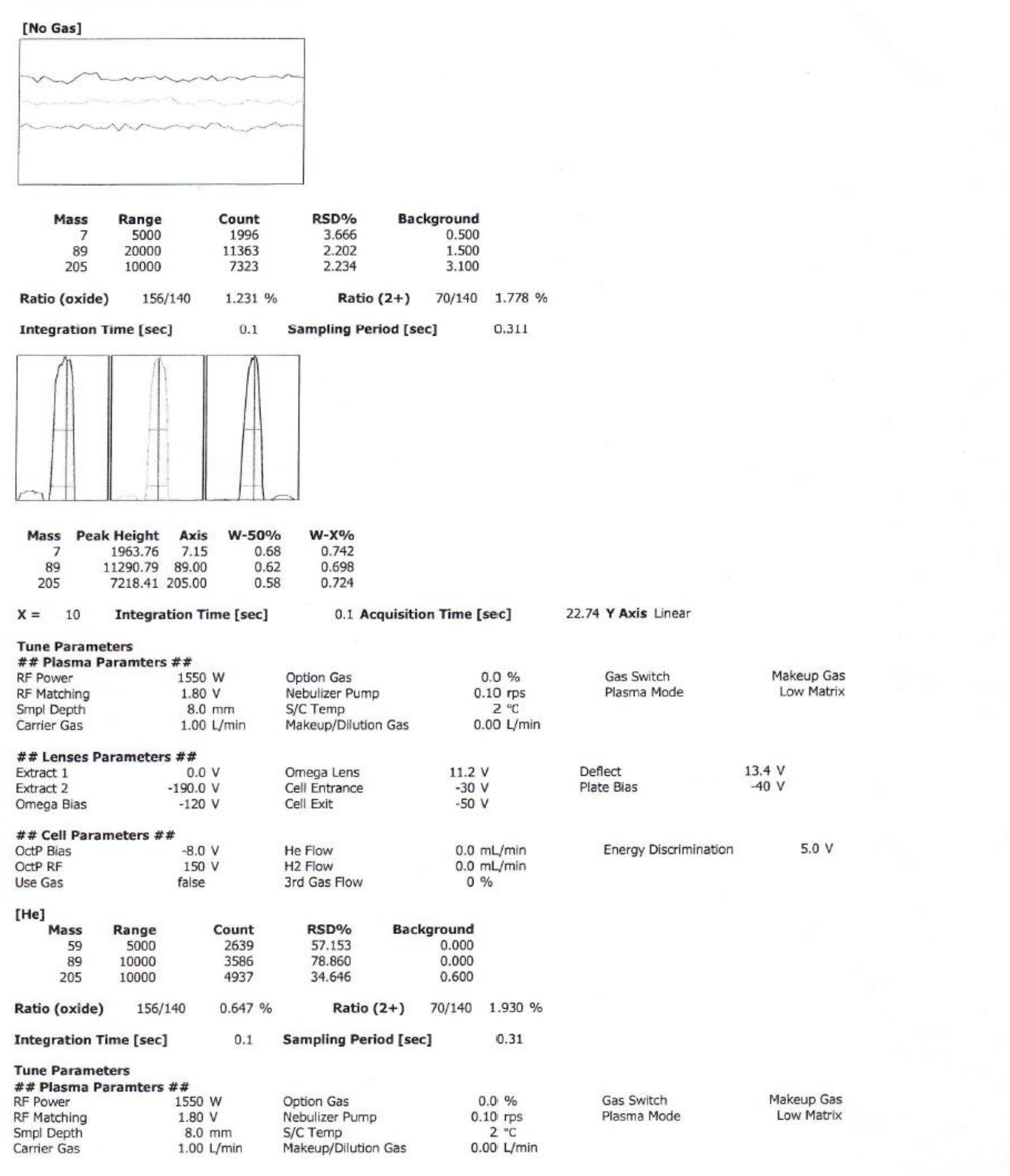
Yahaya, M.I., Mohammad, S. and Abdullahi, B.K. (2009). Seasonal variations of heavy metal concentration in Abattoir dumping site soil in Nigeria. *J. Appl. Sci. Environ. Manag*., vol. 13(4), pp. 9-13.

Yibas, B., Olivier, J., Tekere, M., Mottakeng, T & Jonker, C. Z. (2011). Preliminary health risk analysis of thermal springs in Limpopo Province, South Africa, based on water chemistry. PROCEEDING, Kenya Geothermal conference, November 21-22.

Younger, P.L., Teutsch, G., Custodio, E., Elliot, T., Manzano, M. and Sauter, M. (2002). Assessments of the sensitivity to climate change of flow and natural water quality in four major carbonate aquifes of Europe. In Sustainable groundwater development. Eds. K. M. Hiscock, M. O. Rivett and R. M. Davidson. The Geological Society Publishing House, Bath. pp 303-323.

Zhou, X., Li, R., Zhang, H. and Zhang, L. (2006). Characteristics of natural low pH groundwater in the coastal aquifers near Beihai, China. *Chinese J. Geochemistry*, vol. 25 (1), pp. 228.

Appendix 1: showing the lowest, medium and highest mass number for all the element analysed from ICP-MS (Agilent 7700)



[No Gas]

Mass	Range	Count	RSD%	Background
7	5000	1996	3.666	0.500
89	20000	11363	2.202	1.500
205	10000	7323	2.234	3.100

Ratio (oxide) 156/140 1.231 % **Ratio (2+)** 70/140 1.778 %

Integration Time [sec] 0.1 **Sampling Period [sec]** 0.311

Mass	Peak Height	Axis	W-50%	W-X%
7	1963.76	7.15	0.68	0.742
89	11290.79	89.00	0.62	0.698
205	7218.41	205.00	0.58	0.724

X = 10 **Integration Time [sec]** 0.1 **Acquisition Time [sec]** 22.74 **Y Axis** Linear

Tune Parameters

Plasma Paramters

RF Power	1550 W	Option Gas	0.0 %	Gas Switch	Makeup Gas
RF Matching	1.80 V	Nebulizer Pump	0.10 rps	Plasma Mode	Low Matrix
Smpl Depth	8.0 mm	S/C Temp	2 °C		
Carrier Gas	1.00 L/min	Makeup/Dilution Gas	0.00 L/min		

Lenses Parameters

Extract 1	0.0 V	Omega Lens	11.2 V	Deflect	13.4 V
Extract 2	-190.0 V	Cell Entrance	-30 V	Plate Bias	-40 V
Omega Bias	-120 V	Cell Exit	-50 V		

Cell Parameters

OctP Bias	-8.0 V	He Flow	0.0 mL/min	Energy Discrimination	5.0 V
OctP RF	150 V	H2 Flow	0.0 mL/min		
Use Gas	false	3rd Gas Flow	0 %		

[He]

Mass	Range	Count	RSD%	Background
59	5000	2639	57.153	0.000
89	10000	3586	78.860	0.000
205	10000	4937	34.646	0.600

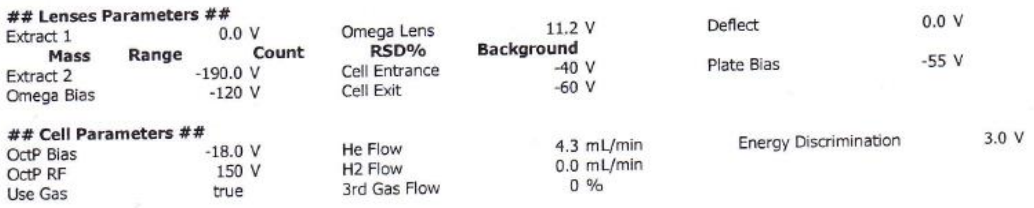
Ratio (oxide) 156/140 0.647 % **Ratio (2+)** 70/140 1.930 %

Integration Time [sec] 0.1 **Sampling Period [sec]** 0.31

Tune Parameters

Plasma Paramters

RF Power	1550 W	Option Gas	0.0 %	Gas Switch	Makeup Gas
RF Matching	1.80 V	Nebulizer Pump	0.10 rps	Plasma Mode	Low Matrix
Smpl Depth	8.0 mm	S/C Temp	2 °C		
Carrier Gas	1.00 L/min	Makeup/Dilution Gas	0.00 L/min		



```
## Lenses Parameters ##
Extract 1                0.0 V     Omega Lens            11.2 V     Deflect                  0.0 V
      Mass     Range          Count     RSD%       Background
Extract 2             -190.0 V     Cell Entrance          -40 V     Plate Bias               -55 V
Omega Bias              -120 V     Cell Exit              -60 V

## Cell Parameters ##
OctP Bias              -18.0 V     He Flow          4.3 mL/min      Energy Discrimination       3.0 V
OctP RF                  150 V     H2 Flow          0.0 mL/min
Use Gas                   true     3rd Gas Flow       0 %
```