University of Venda

Determination of the mineral composition of water and soil samples from Tshipise thermal spring, Mphephu thermal spring and Siloam borehole using inductively coupled plasma mass spectrometry and x-ray fluorescence spectrometry

By

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DEDICATION

I dedicate this work to my mother and friends whose support has been essential in completing this project.

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ABBREVIATIONS AND ACRONYMS

EC	Electrical Conductivity
EU	European Union
GPS	Global Positioning System
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
K_B	Boltzmann constant
K_E	Kinetic Energy
MAC	Maximum Allowable Concentration
RSD	Relative Standard Deviation
S.A. DWAF	South African Department of Water Affairs
SANS	South African National Standards
TDS	Total Dissolved Solids
U.S. EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WHO	World Health Organisation
WQA	Water Quality Association
XRF	X-ray Fluorescence

ABSTRACT

In this study, three sampling sites (Tshipise thermal spring, Mphephu thermal spring and Siloam borehole) in Limpopo Province South Africa were considered for an investigation into the mineral composition of their water and soil samples. Tshipise and Mphephu thermal springs are well developed and located within tourist resorts. On the other hand, Siloam is a borehole on the grounds of a private household. The water is used for various domestic purposes such as laundry, general cleaning of the household and bathing. Water and soil samples from the three sites were collected once per week every week in February 2018. The sampling bottles were spiked with 1M HNO_3 before sampling to keep any metal ions present in the water samples in solution. The soil and water samples were analysed for their chemical composition using X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) respectively. XRF analysis of the soil samples found many major oxides of which SiO_2 made up 63.67%, 85.37% and 46.28% by mass of Tshipise, Mphephu and Siloam soil samples respectively. XRF analysis also showed the presence of dangerous levels of heavy metals such as As, Tl, Pb and V. The analysis of the water samples by ICP-MS found that Tshipise, Mphephu and Siloam mineral water were soft, soft-moderately hard and soft-hard respectively with regards to the water hardness scale according to the United States Geological Survey (USGS) and the Water Quality Association (WQA). Analysis of water samples also found the presence of As, Cd, Cr and V. Arsenic was found to occur at concentrations above the Maximum Allowable Concentration (MAC) set by the World Health Organisation (WHO) (10 $\mu g\ L^{-1}$) for Tshipise, Mphephu and Siloam mineral water (13.63 $\mu g\ L^{-1}$, 15.83 $\mu g\ L^{-1}$ and 20.97 $\mu g\ L^{-1}$ respectively). Water temperatures for the three sites ranged from 38°C (Siloam borehole) to 64°C (Tshipise thermal spring). The pH values were 7.25 (Siloam borehole), 7.40 (Mphephu thermal spring) and 8.67 (Tshipise thermal spring). Due to the presence of As, Tl, Pb, V, Cd and Cr, the mineral water from all three thermal springs is unsafe to consume as it would lead to serious negative health effects some of which are outlined in this study.

Keywords: XRF, ICP-MS, WHO, USGS, WQA, MAC, Tshipise, Mphephu, Siloam

CHAPTER ONE: INTRODUCTION

1.1 Background

Thermal springs are attractive geological features interesting for tourists because of their therapeutic applications (Modabberi et al., 2014). Mankind has been visiting thermal springs for millennia, bathing in and drinking the mineral water, believing in its therapeutic benefits. Mooventhan and Nivethitha (2014) stated that the use of water for various treatments is probably as old as mankind. Toprak et al. (2014) stated that a lot of people have started to visit spars in Turkey for stress reduction. Minerals are the most sought-after component of thermal springs for spa resorts and thermal treatment facilities due to the health-related benefits of the mineral composition of the water (Erfurt-Cooper and Cooper, 2009).

However, thermal spring water has many more uses other than just for curative purposes. Vrba (1996) noted that mineral waters in the Czech Republic are used not only for spa treatment. The mineral waters can be used by industry because of the CO_2 dissolved therein, evaporation to obtain the dissolved salts and local heating during winter. Thermal spring water can also be used for agricultural purposes. The Cunzhou City hot spring in China was used to irrigate rice paddies to enable the cultivation of rice during the winter season (Tuwani, 2011). This study also noted that the mineral deposits associated with thermal springs were of use. For example, North American Indians used deposits such as obsidian and basalt to make tools and weapons.

In this study, three sampling sites (Tshipise, Mphephu and Siloam thermal springs) in Limpopo Province South Africa were considered for an investigation into the chemical composition of their water and soil samples. Tshipise and Mphephu thermal springs are well developed and located within tourist resorts. These resorts are frequented by tourists throughout the year, particularly during the winter months of May-July due to the warm waters. On the other hand, Siloam is a borehole on the grounds of a private household. The water is used for various domestic purposes such as laundry, general cleaning of the household and bathing.

1.2 Problem statement

The thermal springs at Tshipise and Mphephu are visited by many tourists annually. Some (perhaps all) of the tourists do not know the mineral composition of the water they are bathing in and thus could potentially be putting their health at risk, particularly if the water has high levels of heavy metals. Knowing the mineral composition of the water in the Siloam borehole is just as important as water from this borehole is used for domestic purposes. The family is unaware of the mineral composition of this water and thus could be putting their health at risk by using the water. It is therefore imperative that the quantitative and qualitative analysis of the mineral water from the Tshipise thermal spring, Mphephu thermal spring and Siloam borehole is carried out.

1.3 Motivation for the study

Some dissolved minerals in water can be quite toxic to human beings depending on their concentrations. Heavy metals in particular are a concern. They can be introduced to groundwater either naturally (through leaching of rocks and sediments) or through man-made activities such as industry or mining. Some of these minerals can be absorbed through the skin either directly or through cuts and wounds. Tourists come into contact with Tshipise and Mphephu thermal spring water on a regular basis throughout the year, bathing and soaking themselves in the mineral waters. Siloam borehole is used by a private household for various domestic purposes such as washing of clothes, washing of dirty dishes and bathing among others. In such a water scarce area, it is not uncommon for neighbours to this private household to ask for and use this free and accessible source of warm water. It is therefore necessary to investigate which minerals are present in the waters and at what concentration they occur. The results derived from this study will help safeguard the health and wellbeing of all who encounter water from the three thermal springs.

In addition, of all the studies that have been viewed in the literature, only one Durowoju et al. (2016) has carried out a study of the chemical composition of the soil in the immediate vicinity of these springs. As a result, no correlation between the results of the water samples and the surrounding environment (soil) and its possible impact on the thermal springs, particularly in the rainy season, has been carried out in the majority of studies.

1.4 Aim and objectives of the study

1.4.1 Aim of the study

To determine the qualitative and quantitative properties of mineral water (particularly the type of heavy metals present and their levels) in Tshipise thermal spring, Mphephu thermal spring and Siloam borehole water and based on widely reported literature, determine whether these levels pose a threat to human health (both short and long term) or not.

1.4.2 Objectives of the study

- To sample and characterise the water samples from Tshipise thermal spring, Mphephu thermal spring and Siloam borehole in terms of total dissolved solids (TDS), electrical conductivity (EC), temperature and pH.
- To carry out an analysis of soil samples taken near the Tshipise thermal spring, Mphephu thermal spring and Siloam borehole using X-ray fluorescence (XRF).
- To carry out an analysis of water samples obtained from Tshipise thermal spring, Mphephu thermal spring and Siloam borehole using inductively coupled plasma mass spectrometry (ICP-MS).
- To establish a correlation (if any) between concentrations of various components in the soil and water samples from all three thermal springs.
- To compare experimental concentrations to nationally and internationally accepted water standards found in the literature to determine whether the mineral water from these three springs is safe to use.

CHAPTER TWO: LITERATURE REVIEW

2.1 Thermal springs

Thermal springs are sources of water emanating from deep within the Earth's crust. Zhanxue et al. (2017) described thermal springs as being geological features located along deep fault lines. White (2012) defined thermal springs as localized points where groundwater returns to the surface. As such, water from thermal springs is rich in minerals, which dissolve in the water from the surrounding rock strata as the water makes its way to the surface. The exact mineral composition of thermal spring water depends on the subterranean geology beneath the thermal spring from which the water has been sourced. Waring (1965) stated that spring water with an average temperature above the mean annual temperature of the area in which the spring is found may be classed as thermal. In addition, Waring (1965) noted that thermal springs are common in volcanically active areas and areas where rocks are faulted and folded.

This study focused on three thermal springs in South Africa; Tshipise, Mphephu and Siloam. All three sites are in the mountainous Soutpansberg region of Limpopo Province. Two of the thermal springs (Tshipise and Mphephu) are now well-developed tourist resorts, whereas Siloam is a private borehole on the grounds of a private residence.

2.1.1 Tshipise thermal spring

The Tshipise thermal spring is in the Limpopo Province of the Republic of South Africa. The spring is located within the Honnet nature reserve, surrounded by fairly flat terrain (Olivier et al., 2011). With a mineral water temperature of 65°C, the Tshipise thermal spring is classified as "hot". Tshipise resort has numerous chalets, a restaurant and a site where families can camp to mention but a few. The actual spring has been changed into a tourism feature. A concrete structure with glass windows has been constructed around the source. This allows visitors to view the water as it bubbles from the ground and the variety of multicoloured algae growing on the sides and floor of the spring. The Tshipise thermal springs are visited annually by tourists for the perceived health benefits of soaking oneself in the water. In addition to the perceived health benefits derived from bathing in the mineral water, many tourists flock to bath in the thermal waters purely for relaxation purposes.

Figure 2.1 shows a tap connected to the reservoir of the Tshipise thermal spring. The samples were drawn from this tap. The tap is connected to the Tshipise thermal spring reservoir which has been concealed by the stone masonry structure shown. In the top right corner of the figure is a heat resistant glass shield through which visitors can view the reservoir. The heat resistant glass shield is itself covered by a metallic grill to protect it from scratches or any external damage by visitors.

Figure 2.1 Tshipise thermal spring reservoir tap from which samples were drawn.

2.1.2 Mphephu thermal spring

Mphephu thermal spring is in the Soutpansberg mountainous area of Limpopo Province, South Africa. Tekere et al. (2012) stated that Mphephu was a well-developed resort and that the reservoir of mineral water could be easily accessed by both community members and wildlife. The spring is at the foot of a mountain and receives a lot of vegetation litter, which comes from the overhanging branches of trees surrounding the reservoir of the spring. When the leaves and other biomass fall into the reservoir, the combination of the warm mineral water and micro-organisms rapidly decompose the biomass. The decomposed biomass releases minerals and other nutrients into the water. Some of the biomass falls onto the soil immediately surrounding the spring and is decomposed by micro-organisms present in the soil.

Being at the foot of a mountain, Mphephu thermal spring is affected by surface run-off during the rainy season. When it rains, water cascades down the side of the mountain towards the spring carrying with it soil, leaves, grass and other organic and inorganic material. The spring is very shallow, not more than 30 cm in depth in places. The resort describes the mineral water from Mphephu as “hot.” In reality, the water is luke-warm. A hand can be submerged into the reservoir for an indefinite period without feeling any discomfort or being scalded. There are two distinct points in the reservoir where water bubbles up gently to the surface.

Figure 2.2 shows the Mphephu thermal spring reservoir. The reservoir is shallow and spring water bubbles up slowly on the far left of the pool. The trees surrounding the spring sometimes drop leaves into the pool. The soil samples were collected just next to the reservoir. A stone masonry structure has been built up around the spring to contain the mineral water bubbling up from the Earth’s surface, forming a crystal clear shallow pool. The pool is a magnet for a lot of insects, in particular bees, that were buzzing all around the pool’s edges when the samples were collected.

Figure 2.2 Mphephu thermal spring reservoir.

2.1.3 Siloam borehole

Siloam borehole is also located in the Soutpansberg mountainous area of Limpopo Province. However, Siloam is not an open-air spring. There is no distinct reservoir where water bubbles from underground and is collected in a pool. Siloam is a borehole located on the property of a private residence. The water is piped and is used for various domestic purposes such as bathing, washing dishes, washing clothes, cooking among others. Next to this private residence is another source for Siloam mineral water. According to residents, this second source, also located on the grounds of another private residence belonging to a Mrs Anna Nengudza, dried up several years ago.

Siloam borehole is situated on private property and is used as a source of heated water for the household. There are two buckets behind the man in the image that, on the day of sampling, were being used to collect mineral water for laundry purposes. Connected to the borehole is a black pipe that is used to fill the buckets with the warm water.

Figure 2.3 Siloam borehole.

2.2 Origins of mineral water in thermal springs

Most of the water that emerges at thermal springs is meteoric in nature, that is, it originally fell as rain or snow on the surface of the Earth (Kharaka et al., 2002). Skopljak and Vlahovic (2011) carried out a study of the origin of mineral waters in Kiseljak, Bosnia and Herzegovina. The study showed that the water is of atmospheric origin (falling originally as either rain or snow). The study also showed that after descending into the ground, the water is enriched with CO_2 and minerals before rising to the surface again. Figure 2.4 shows a generalised diagram of thermal springs whose mineral water is meteoric by origin. After it rains, the water seeps into the ground. The deeper the water goes, the hotter it gets. This is shown in the figure by a gradual increase in temperature from 200°C to 300°C as the water (now steam) approaches the magma. The water is heated and returns to the surface of the Earth through cracks or faults in the ground. The deeper the water seeps into the ground, the more it is heated and thus the hotter the mineral water will be when it returns to the surface once more. When the water returns to the surface, it will be as steam. The water can also return to the surface as either warm, hot or boiling liquid water.

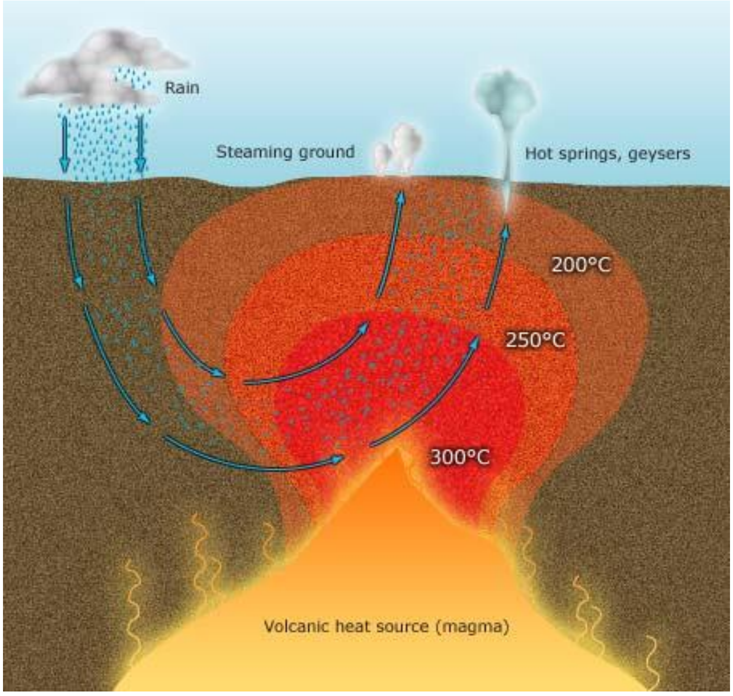


Figure 2.4 Meteoric mineral water in thermal springs (Stewart, 2006).

As the water heats up as it descends deep underground, the water molecules experience an increase in kinetic energy (K_E) (Equation 1), where T is the temperature. The K_E of a substance is directly proportional to the T of the particles making up that substance. This is shown in Equation 1 below. The equation shows that an increase in temperature results in an increase in kinetic energy.

$$K_E \propto T \qquad eqn\ 1.$$

This increase in kinetic energy increases the rate of dissolution of minerals in surrounding rocks as the rapidly moving water molecules collide with the minerals in the rocks. As a result, when the water returns to the surface, it is rich in minerals that have dissolved from the surrounding rock strata.

When the proportionality symbol is replaced with an equal sign, mathematical laws dictate that a constant must be inserted into the equation. This is shown in Equation 2 below.

$$K_E = k \cdot T \qquad eqn\ 2.$$

The constant in this case is the Boltzmann constant (k_B). Replacing k in Equation 2 with the Boltzmann constant yields Equation 3.

$$K_E = \frac{3}{2} \cdot K_B \cdot T \qquad eqn\ 3.$$

2.3 Typical inorganic components found in thermal spring water

Mineral water from thermal springs is rich in inorganic components. As stated in section 2.1, many of these chemical species are derived from surrounding rocks. The mineral water encounters these rocks on its way to the surface, dissolving any soluble minerals found in the rocks. Because mineral water originates from deep within the Earth's crust, the water is very often of a very high temperature. This increases the rate of dissolution of any minerals in surrounding rocks and in turn creates a lot of steam. Depending on the steam pressure, this could create an explosive release of the water when it finally reaches the surface.

Examples of such inorganic components include:

- Anions such as F^-, Cl^-, Br^-, SO_4^{2-}, PO_4^{3-} and CO_3^{2-}
- Cations such as Na^+, Ca^{2+}, Mg^{2+}, K^+, Li^+ and Ba^{2+}
- Heavy metals such as Cd, As, Pb, Cr, Tl and Hg. These are generally toxic and can exist in a variety of oxidation states.

These inorganic components can also be introduced into thermal spring reservoirs by man-made activities such as agriculture, mining and industrial waste. Acid mine drainage is a common source of groundwater pollution as it contains high concentrations of heavy metals such as cadmium, cobalt, copper, molybdenum, zinc and sometimes radionuclides (Oelofse, 2008). Saracino and Phipps (2002) noted that groundwater systems feeding thermal springs can also be contaminated by pesticides, seawater intrusion, landfills, hazardous waste disposal sites, underground storage tanks, urban storm water runoff, mine drainage and oil-field brines.

2.4 Classification of thermal springs according to temperature

Zhijie (2017) classified thermal springs into three categories based on mineral water temperature, the annual mean maximum temperature of the earth and the local annual average temperature. The three categories used to classify thermal springs according to temperature were as follows:

- Warm springs
- Hot springs
- Boiling springs

2.4.1 Warm springs

Whilst there is no universally accepted guideline to classifying thermal springs (Pentecost et al. 2011), Liao (2018) defines warm springs as thermal springs whose water temperature ranges from 35°C to 45°C. In a study carried out by Wamalwa et al. (2010) on the Saratoga and Tecopa thermal springs, warm springs were simply defined as having a much lower water temperature than hot springs. The study further stated that the water temperature of Saratoga and Tecopa thermal springs was 30°C and 41°C respectively. Awadh and Al-Ghani (2014) carried out a study on eleven sulphurous springs in the west of Iraq for balneotherapy, drinking, irrigation and aquaculture purposes. It was concluded that the springs were warm in nature, having a water temperature range of 27-30°C.

A lack of fixed guidelines in defining thermal springs is a problem in the study of thermal springs globally. For example, whilst Wamalwa et al. (2010) described the water at Saratoga thermal springs as warm due to a water temperature of 30°C, Bonny and Jones (2007) defined stinking springs, a sulphur spring system in North-western Utah, United States as warm, even though it has a water temperature of 48°C.

2.4.2 Hot springs

Hot springs are defined as having waters emerging from the Earth’s crust with a temperature more than the core human body temperature of 36.7°C (Pentecost et al., 2003). Kresic (2010) defined hot springs as having a water temperature higher than 37°C. Pentecost (2005) noted that, while the term “hot springs” suggests boiling waters, explosive emissions of steam and volcanism, many exit temperatures are far lower than the boiling point of water. However, the same authors noted that the exit temperatures remained elevated above the mean air temperature of other types of springs. The exact mineral composition of hot spring water depends on the underlying geology and thus the geographical location of that hot spring. Normally, hot springs form in areas with high volcanic activity.

Hot springs, however, are not only related to volcanic activity. Baioumy et al. (2015) determined that, due to the sodium bicarbonate nature of the waters and their low sulphate concentrations, the hot springs of West Malaysia were of non-volcanic origin.

Different countries classify hot springs according to different criteria. For example, Subtavewung et al. (2005) classified hot springs in Thailand according to three criteria:

- Temperature (hyperthermal springs (50°C-99°C) and thermal springs (37°C-50°C)).
- pH values (neutral (6-7.5), weak alkaline (7.5-9) and alkaline (9-10)).
- Usage (power plant, tourism, consumption and unutilized).

A lack of internationally accepted guidelines for classifying hot springs (and indeed other types of thermal springs) makes the study of hot springs difficult as each individual country may have its own unique classification.

2.4.3 Boiling springs

Boiling springs are thermal springs with a water temperature often more than 100°C. Poorter et al. (1989) carried out a study on Sirung volcanic boiling spring in Indonesia, and found that apart from being an extremely chloride rich acid brine, the water had a temperature of 240°C. Saemundsson (2013) classified thermal springs with a reservoir temperature of <190°C at a depth of 1 km as boiling springs. Costa et al. (2009) defined boiling springs as thermal springs with a temperature >73°C. Brombach et al. (2000) defined Bouillante geothermal reservoir in Guadeloupe as boiling due to its temperature of 250°C. The same study went on to define the La Soufriere geothermal fields as boiling due to the temperature of the water emanating from them (190°C-215°C). Some of these aqueous solutions had temperatures of up to 260°C (Brombach et al., 2000).

2.5 Additional classification of thermal springs

Thermal springs can be classified by other criteria and not just the temperature of their water. Andreassi and Flori (1996) classified the thermal springs of Italy according to the mineral composition of their waters. They adopted the following criteria: Salty, sulphurous, bicarbonated, sulphated, carbonic, arsenical and ferruginous.

Salty thermal springs are rich in ions such as Na^+ and Cl^-, that is, such waters are very rich in sodium chloride. Water that has a very high concentration of NaCl is referred to as a brine. Sulphurous thermal springs are rich in the dissolved gas hydrogen sulphide, a gas which is toxic. It is typically found in hot springs and in ground water (Chou, 2003). Bicarbonated thermal springs are springs whose water is reach in bicarbonates. The higher the concentration of carbonates in the water, the higher the degree of “carbonate hardness” of the water. Sulphated thermal springs are springs rich in sulphates. Minerals that are main sources of sulphates in water are barite ($BaSO_4$), epsomite ($MgSO_4{\cdot}7H_20$) and gypsum ($CaSO_4{\cdot}2H_2O$) (WHO, 2004).

Carbonic thermal springs are springs rich in dissolved carbon dioxide. When carbon dioxide dissolves in water, it forms carbonic acid. This is a weak inorganic acid and therefore, the pH of such waters is slightly acidic. Arsenical thermal springs are rich in the heavy metal arsenic. Arsenic contamination of groundwater can be either natural or man-made. Arsenic contamination in drinking water has a detrimental effect on human health which profoundly affects the quality of life (Yunus et al., 2016). Ferruginous thermal springs are rich in iron. Sources of iron can include iron bearing minerals such as iron sulphide and iron rich clay minerals (Mansoor, 2012). Mansoor also stated that anthropogenic sources of iron include industrial effluents, landfill leakages and acid mine drainage.

Petraccia et al. (2006) classified thermal springs further according to the biological activity of their waters, adopting the following classification: Diuretic waters, cathartic waters and waters with antiphlogistic properties.

Diuretic thermal springs are springs whose water can increase the amount of sodium that is excreted from the body in urine (Mandal, 2014). This has the effect of increasing the volume of urine and the frequency of urination. This aids in the excretion of any toxins that may be present in the body via urination.

Thermal springs that have water with cathartic abilities have the effect of decreasing the absorption of substances by accelerating the expulsion of the toxin from the gastrointestinal tract (Clinical toxicology, 2004).

Antiphlogistic waters have anti-inflammatory effects (Lucaska et al., 1982). Such water can therefore be used to reduce pain and fever (Dinarello, 2010). This author also stated that antiphlogistic waters can be used to reduce inflammation.

2.6 Uses of thermal springs

The uses of a thermal spring very much depend on the mineral composition of the water emanating from the spring. LaMoreaux and Tanner (2012) highlighted the various therapeutic benefits of thermal spring water depending on its mineral composition:

- Carbonated or bicarbonated thermal spring water stimulates digestive secretions, neutralizes hyperacidity and has diuretic effects.
- Thermal spring water with a high calcium sulphate content relieves kidney irritation, has a diuretic effect and increases kidney function.
- Thermal spring water with a high sodium bromide and sodium iodide content stimulates the activity of the lymphatic system and helps eliminate metallic poisons in the system.

Albu et al. (2012) further reinforced the notion that thermal spring water has many therapeutic benefits, by stating that mineral water rich in sulphates has the following health benefits:

- Increase in influx of bile.
- A 40% increase in diuretic effects (increased passing of urine).
- An increase in the volume and weight of faecal matter.
- Various metabolic increases such as excretion of urea, calcium, manganese and potassium.
- Bactericidal effect on various skin conditions caused by streptococcus bacteria.

The first four benefits are only realised after ingestion of the sulphate rich mineral water. Altman (2000) stated that the high levels of sulphates and bicarbonates in thermal spring water from San Pellegrino, Italy, help control the acidic level of gastric juices and stimulate digestive processes.

2.7 Adverse effects of certain minerals on human health

Although the health benefits of mineral water from thermal springs have been abundantly highlighted by numerous studies (Section 2.9), some elements in mineral water can be extremely toxic to human health (depending on their concentration). Such elements include but are not limited to; As, Pb, Tl, Cd and Hg.

As a result, knowing the composition of mineral water from thermal springs is of utmost importance, to safeguard the health and wellbeing of tourists and locals who frequent them.

Exposure to As leads to its accumulation in tissues such as skin, hair and nails, resulting in various negative effects on health. Such negative health effects include hyper-pigmentation, keratosis, cardiovascular disease, neuropathy, cancer, suppressed hormone regulation and hormone mediated gene transcription, foetal loss, premature delivery and decreased birth weights of infants (Kapaj et al., 2007). Chowdhury et al. (1999) noted that As can cause skin cancer, lung cancer and kidney problems. Huy et al. (2014) determined that As can cause skin, lung and bladder cancer. The same authors also noted that As can also adversely affect the cardiovascular, pulmonary, nervous, endocrine and reproductive systems. The World Health Organisation (WHO) has set the maximum allowable concentration (MAC) for As at 10 µg L^{-1} (Table 2.1).

Rosen (1995) stated that a direct link has been established between low-level Pb exposure during early childhood development and deficits in neurobehavioral-cognitive performance evident late in childhood through adolescence. A consistent link between low-level Pb exposure to children in China and deficits in IQ, neurobehavioral development and physical growth was established (Xiao-ming et al., 1996). The European Union (EU) sets the MAC of Pb in public drinking water at 10 µg L^{-1} (Table 2.1). High concentrations of Pb damage organs and organ systems, most notably the central nervous system (Tong et al., 2000). Neurological, reproductive, renal and haematological systems are susceptible to adverse effects of exposure to Pb (Juberg, 2000). Hutton (1987) noted that Pb poisoning in children causes inattention, cognitive difficulties and impaired movement.

Following low level environmental exposure to Tl, non-specific symptoms such as tiredness, sleep disorders, headaches and muscle pains were reported (Kazantzis, 2000). Neuropsychological tests on two patients with acute Tl intoxication were carried out (Yu-Tai et al., 2006). The tests revealed that the patients suffered from memory impairment, confusion, disorientation, hallucination, anxiety, depression and lack of attention. The long-term effects of Tl poisoning include change in blood chemistry, damage to the liver, kidney, intestinal and testicular tissue (Maluszynski, 2009). The same author also noted that Tl has carcinogenic, mutagenic and teratogenic effects. Roper (1992) ascertained that Tl can affect the nervous system, lung, heart, liver and kidney. In addition, Roper (1992) also noted that Tl can cause temporary hair loss, vomiting and diarrhoea. The U.S. EPA set the MAC for Tl in water at 0.5 µg L^{-1} (Table 2.1).

Cadmium poisoning leads to chronic kidney disease and renal failure (Johri et al., 2010). Chronic exposure to low-level Cd has been associated with renal failure, diabetic renal complications, osteoporosis (weakening of bones), inhibited blood pressure regulation and increased cancer risk (Satarug and Moore, 2004). Bernhoft (2013) stated that Cd poisoning leads to a decrease in bone density (particularly in children), hypertension, diabetes, a weakened cardiovascular system, decreased attention levels and impaired memory function. The same author also stated that Cd poisoning can lead to kidney failure, bone demineralization, impaired lung function and increased risk of lung cancer. The Water Quality Association (WQA) (2018) set the MAC for Cd in water at 5 µg L^{-1} (Table 2.1).

Mercury is yet another heavy metal that is toxic to life forms at trace concentrations. Mercury particularly affects the central and peripheral nervous systems of children (including foetuses) and causes a number of health problems such as kidney damage, irregular heartbeats, excessive sensitivity to external stimuli, shortness of breath, chest pains, weakness and fatigue (Tchounwou et al., 2003). Mercury can be introduced into surface water bodies by either Hg mining or Au mining activities where

Hg is used in the recovery of Au (Domagalski, 2001). The same author also noted that certain species of fish are a major source of Hg poisoning in the form of methylmercury (CH_3Hg^+). Mirlean et al. (2003) noted that the principal causes of mercury pollution in estuarine sediments in Patos Lagoon, Brazil, were insufficient control on waste collecting and the absence of sewage treatment. The South African Department of Water Affairs (S.A. DWAF) has set the MAC for Hg in water at 1.0 µg L^{-1} (Table 2.1).

Table 2.1 shows a summary of MACs of five heavy metals (As, Pb, Tl, Cd and Hg) as set by five agencies. The MACs are different because different scientific bodies set these values and each body will adopt its own measurement parameters. The MACs in the table are very low because the five heavy metals shown are extremely toxic at trace concentrations. Thallium has the lowest MAC (0.5 µg L^{-1}) as it is extremely toxic. Exceeding this MAC would be detrimental to not only human health but to the environment at large.

Table 2.1 MACs for select heavy metals

Heavy metal	MAC (µg L^{-1})	Body/Reference
As	10.0	WHO
Pb	10.0	EU
Tl	0.5	U.S. EPA
Cd	5.0	WQA
Hg	1.0	S.A. DWAF

In addition to cations, water can also contain a number of different anions. Examples of these include; F^-, Cl^-, SO_4^{2-} and NO_3^-. Unlike heavy metals, a lot of anions are non-toxic and are required for the normal functioning of a number of life processes. Kelly et al. (2012) stated that Cl^- is non-toxic to humans. The same authors go on to state that even though Cl^- is non-toxic to humans, a drinking water standard of 10 mg L^{-1} has been set for it by the South African government (Table 2.2). This high MAC emphasises the non-toxicity of Cl^-, unlike heavy metals whose MACs are in the region of parts per billion, due to their toxicity even at trace concentrations. Addiscott and Benjamin (2006) stated that NO_3^- is essential for human health, not a threat. The study carried out by Addiscott and Benjamin (2006) showed that NO_3^- is converted to NO_2^-

in the human body, which in turn is converted to NO. The study stated that NO is effective against certain pathogenic bacteria and safeguards against dental caries and fungal skin infections. Sulphate is also non-toxic to humans. Dawson (2013) stated that because the human foetus cannot generate its own SO_4^{2-}, SO_4^{2-} concentrations in the mother's blood increase from about mid-gestation. This is essential for the normal development of the foetus.

However, F^- can pose serious health risks to human beings if it occurs at concentrations exceeding its MAC (Table 2.2). High F^- concentrations in water can lead to dental fluorosis. In dental fluorosis, the subsurface enamel all along the tooth becomes increasingly porous (hypo mineralized), and the lesion extends toward the inner enamel (Fejerskov et al., 1994). In addition, excessive F^- intake was associated with a lower intelligence in children (Li et al., 1995). Thole (2013) noted that skeletal fluorosis is characterised by weakening of bones and malformation, muscle fibre degeneration, low haemoglobin levels, red blood cell deformities, excessive thirst and headaches. The same author also stated that skeletal fluorosis manifests itself as skin rashes, depression, gastrointestinal problems, urinary tract malfunction, nausea, abdominal pains, a tingling sensation in fingers and toes, reduced immunity and neurological manifestations.

Table 2.2 shows a summary of the MACs that have been set for four anions by four different bodies; The WHO, EU, the Netherlands and South Africa. The MACs are different because they have been set by different bodies. All four bodies have set very low MACs for F^- due to its adverse health effects on the human body when these concentrations are exceeded. The other anions have comparatively very high MACs. This is an indication of their non-toxicity relative to F^-.

Table 2.2 MACs of select anions

Anion	WHO mg L^{-1}	EU mg L^{-1}	Netherlands mg L^{-1}	South Africa mg L^{-1}
NO_3^-	50	50	50	10
Cl^-	250	250	150	200
SO_4^{2-}	500	250	150	400
F^-	1.5	1.5	1.1	1.0

2.8 Water hardness

Water safety is not the only concern for legislators around the world. Water quality is also essential. One of the parameters looked at with regards to water quality is water hardness. Water hardness is a physico-chemical property of water depending on the presence of alkali earth metals, mainly Ca and Mg in water (Oliveira-Filho et al., 2014). There are many other physico-chemical properties of water. Gordolla et al. (2007) stated that such properties can include but are not limited to: freezing, melting and boiling point of water, surface tension of water, specific heat capacity of water, Ph, temperature, total dissolved solids, electrical conductivity and dissolved oxygen. Some of these physico-chemical properties are widely available in literature and are due primarily to the inter-molecular hydrogen bonding that exists between water molecules. However, some physico-chemical properties vary according to the water source.

Water Ca and Mg result from the decomposition of Ca and Mg aluminosilicates and, at higher concentrations, from the dissolution of limestone, magnesium limestone, magnesite, gypsum and other minerals (Kozisek, 2003). The same author went on to state that in underground and surface waters, Ca and Mg are mainly present as Ca^{2+} and Mg^{2+}, with Ca and Mg levels varying from tens to hundreds of mg L^{-1} and from units to tens of mg L^{-1} respectively. Min et al. (2018) stated that hardness in water leads to scaling of pipes, boilers and odd tasting drinking water and is caused by dissolved minerals, mainly calcium and magnesium compounds.

There is increasing research, however, that shows that apart from affecting the quality of water, a high concentration of Ca in drinking water can have negative health effects. Chatterjee et al. (2012) noted that water hardness has resulted in a 50% increase in urinary Ca leading to the formation of kidney stones. The same study went on to highlight that people living in the Western Indian states of Gujarat, Maharashtra and Rajasthan (which have high salinity in ground water) are highly prone to the formation of urinary stones. Bellizzi et al. (1999) stated that ingesting hard water carried with it a significantly high risk for the formation of calcium stones. The same study also noted a 50% increase of urinary calcium concentration in participants of the study.

However, there is significant disagreement in literature as to whether there is a direct correlation between water hardness and the formation of kidney stones. In his review of findings generated by the WHO, Henney (2011) stated that the WHO had concluded that hard water not only posed no risk of kidney stones to populations at large but, it may prevent the formation of kidney stones. The same author went on to state that the WHO had further concluded that water rich in Ca had several health benefits such as prevention of osteoporosis and rickets, less hypertension and stroke and decreased insulin resistance. Henney (2011) went on to further state that the low Ca content in the diet could actually lead to an increased risk of colorectal cancer, cardiovascular disease and obesity. Costi et al. (1999) carried out a study on post-menopausal women and noted that a lifelong daily Ca intake by drinking water with a high Ca concentration was essential to maintain bone mass after menopause. The same study went on to note that women who had ingested water with a low Ca content had a significantly lower bone density than women who had ingested water with a high Ca content.

Table 2.3 shows the water hardness classifications adopted by the WQA (2018), the United States Geological Survey (USGS) (2016), Rand Water (2000) (a South Africa based company) and Oliveira-Filho et al., (2014). Water hardness is classified in four ways; soft, moderately hard, hard and very hard. Both the WQA (2018) and USGS (2016) are in agreement with all the four different classifications. This is probably because both bodies are U.S. based bodies and therefore are more likely to adopt similar classifications for water hardness. The WQA (2018) and USGS (2016) adopt the classifications shown in Table 2.3 for both Ca^{2+} and Mg^{2+}. The 2014 study by Oliveira-Filho and Rand Water base their classifications on mg L^{-1} of $CaCO_3$. The table shows that by and large, the water hardness classification concentrations adopted by Rand Water are less stringent than the other three references, particularly when classifying moderately hard and hard water. However, of all four references, Rand Water has the strictest soft water classification concentration range.

Table 2.3 Water hardness classification based on mg L^{-1} of $CaCO_3$, Ca^{2+} and Mg^{2+}.

Water hardness classification	Oliveira-Filho et al., 2014	WQA	USGS	Rand Water
Soft	0-75	0-60	0-60	0-50
Moderately hard	75-150	61-120	61-120	150-200
Hard	150-300	121-180	121-180	200-300
Very hard	>300	>180	>180	>300

Table 2.4 shows the allowable concentrations of Ca, Mg and their compounds in water as set by five different references; The European Commission, Hungary, Poland, South African National Standards (SANS) and a 2003 study carried out by Kozisek. Hungary and Poland gauge water hardness according to mg L^{-1} of CaO and $CaCO_3$ respectively. The European Commission, SANS and Kozisek (2003) measure water hardness according to mg L^{-1} of Ca^{2+} and Mg^{2+}. Table 2.4 shows that the South African National Standards has adopted a much less stringent guideline for Ca^{2+} and Mg^{2+} concentrations in water relative to the European Commission and Kozisek (2003).

Table 2.4 Acceptable levels of water hardness based on mg L^{-1} of Ca^{2+}, Mg^{2+}, CaO and $CaCO_3$.

Chemical species	European Commission	Hungary	Poland	SANS	Kozisek (2003)
Ca^{2+}	<100	n/a	n/a	<150	40-80
Mg^{2+}	<50	n/a	n/a	<70	20-30
CaO	n/a	50-350	n/a	n/a	n/a
$CaCO_3$	n/a	n/a	60-500	n/a	n/a

*n/a (not available)

2.9 International studies

Research was conducted to determine the arsenic concentration in the hot springs of Bahia Concepcion, Baja California peninsula, Mexico. High arsenic concentrations

(0.15 to 0.78 mg L^{-1}) were measured in water discharged from hydrothermal vents (Villanueva-Estrada et al., 2013). Pena-Reyes et al. (2015) conducted a study into the occurrence of natural arsenic in groundwaters from alpine springs in upper Valtellina, northern Italy. The study determined that all the springs analysed contained both As (III) and As (V) oxidation states. Water samples from thermal springs in the Bolivian Altiplano, along the Andes mountain range, were found to contain arsenic concentrations in the range 7.80 to 65.30 µg L^{-1} (Ormachea-Munoz et al., 2015). Chloride concentrations in water samples taken from thermal springs in the Cascade mountain range in the U.S, were found to have concentrations in the range of 64 to 19000 mg L^{-1} (Cullen et al., 2015).

Sracek et al. (2015) conducted a survey of groundwater from six geothermal springs in Namibia. The results showed high concentrations of dissolved fluoride, with values of up to 18.9 mg L^{-1}. A study on a number of hot springs in South Korea was carried out (Yoon et al., 2012). The study showed the presence of ions such as F^- (0.7 to 16.8 mg L^{-1}), SO_4^{2-} (4.5 to 950 mg L^{-1}) and Cl^- (4.83 to 15380 mg L^{-1}). A study into the chemical composition of hot springs in Japan was conducted (Sano et al., 2008). The study showed the presence of elements such as Na (1.6 to 152 mg L^{-1}), K (0.8 to 78.2 mg L^{-1}), Mg (0.3 to 117 mg L^{-1}), Ca (0.7 to 124 mg L^{-1}), Fe (1.9 to 8.6 mg L^{-1}), Al (2.2 to 187 mg L^{-1}) and Mn (0.2 to 11.7 mg L^{-1}). In addition, the study also found the presence of Cl^- (13.8 to 868 mg L^{-1}) and SO_4^{2-} (421 to 2817 mg L^{-1}).

Kikawada et al. (2004) carried out a study on the chemical composition of hot spring water in Japan. The study showed the presence of Na (138 mg L^{-1}), K (80.4 mg L^{-1}), Mg (65.4 mg L^{-1}), Ca (115 mg L^{-1}), Fe (9.33 mg L^{-1}), Al (64.9 mg L^{-1}), Mn (2.97 mg L^{-1}), Si (128 mg L^{-1}), Cl^- (945 mg L^{-1}) and SO_4^{2-} (1786 mg L^{-1}). A study on cold and warm springs in Iran was done (Sharifi et al., 2016). The study showed the presence of Ca (55.11 to 761.48 mg L^{-1}), Mg (3.65 to 227.86 mg L^{-1}), Na (5.06 to 423.02 mg L^{-1}), K (0.78 to 65.68 mg L^{-1}) and Cl^- (7.09 to 857.96 mg L^{-1}). Kundu et al. (2001) ascertained the chemical composition study of hot spring water in Nayargarh district, India. The study showed the presence of F^- to range from 12 to 14.2 mg L^{-1}. Cl^- and SO_4^{2-} were found to range from 171 to 192 mg L^{-1} and 16.1 to 22.8 mg L^{-1} respectively.

2.10 National studies

Faniran et al. (2001) conducted a study into the chemical properties of water samples collected from Isinuka springs, in the Port St Johns area of the Eastern Cape province. The samples collected exhibited very high concentrations of chloride and ammonium, which exceeded the maximum permissible levels recommended for drinking water. The study also showed that the nitrate and nitrite ions were present at levels far below the critical value of 10 mg L $^{-1}$. A study into the fluoride concentration of the Namaqualand thermal groundwater system was done (Abiye et al., 2018). The study found that the concentration of fluoride in the water samples ranged between 0.28 mg L^{-1} to 7.95 mg L^{-1}.

Douglas (2006) ascertained the chemical composition of Florisbad spring water in the Free State Province. The study found the water samples to be completely saturated by $CaCO_3$. A study of the chemical composition of deep groundwater in the Karoo basin, Northern Cape Province was carried out (Miller et al., 2015). The study found that Cl^- concentrations ranged from 200 mg L^{-1} to 1000 mg L^{-1}.

Baiyegunhi et al. (2014) carried out a study on the chemical composition of Aliwal North Hot spring in the Eastern Cape Province. This study confirmed that the element thorium was below the World average hazardous threshold of 7.4 mg L^{-1}. Wu (2009) conducted a study on springs in the Western Cape Province such as Kirsten, Albion and Newlands. The study showed the presence of a variety of species such as Sr, Ba, Al, Cr, Mo, Mn, Fe, Ni, Cu, Si, Zn, Cd and Pb. Silicon occurred with the highest concentration in all springs, the highest concentration being 4.158 mg L^{-1} from Kirsten spring. All other elements were in trace concentrations. An investigation into the salinity of thermal springs around South Africa was done (Mazor and Verhagen, 1983). The study revealed that springs such as Malmesbury, Aliwal Noord and Florisbad had salinity concentrations in the range 936-2364 mg L^{-1}. The same study showed that springs such as Lilani, Natal Spa and Olifants have a salinity concentration of 90-432 mg L^{-1}.

2.11 Local studies

Many studies into the chemical composition of water samples collected from thermal springs have also been conducted in Limpopo province, South Africa.

A study was conducted into the mineral composition of water samples taken from Tshipise, Mphephu, Siloam, Minwamadi, Sagole, Moreson, Evangelina and Die Eiland thermal springs. It was ascertained that the water samples had sodium, potassium, calcium, magnesium, fluoride, nitrate, chloride, sulphate, phosphate and carbonate (Olivier et al., 2011). Shabalala et al. (2015) carried out investigations into the chemical composition of water samples collected from Tshipise, Dopeni, Siloam, Mphephu and Sagole thermal springs. The samples were collected during the winter and summer months and were found to contain calcium (4.47 mg L^{-1}), silicon (3.60 mg L^{-1}), potassium (4.02 mg L^{-1}) and magnesium (0.12 mg L^{-1}), among others. Olivier et al. (2008) investigated the chemical composition of water samples collected from Warmbad, Loubad, Vischgat, Die Oog, Rhemardo and Libertas thermal springs. The samples were found to contain sodium (55.95 mg L^{-1}), potassium (6.13 mg L^{-1}), calcium (36.13 mg L^{-1}) and magnesium (3.30 mg L^{-1}), among others.

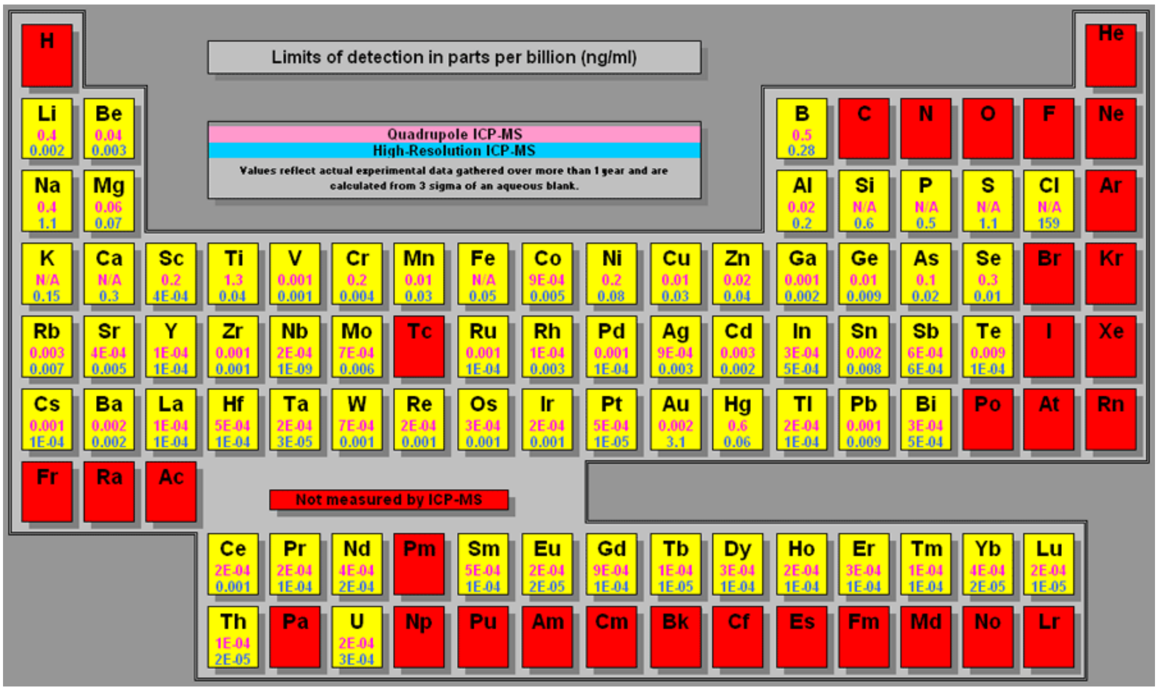
Tekere et al. (2011) determined that the water from Siloam hot spring contained heavy metals such as arsenic (0.3 µg L^{-1}), chromium (1 µg L^{-1}), lead (0.1 µg L^{-1}) and mercury (0.5 µg L^{-1}). The same study also found that the water samples contained lighter elements such as sodium, potassium, calcium and magnesium. Anions such as fluoride, chloride, nitrate, sulphate, phosphate, carbonate and bicarbonate were also present in the Siloam water samples. A study on three thermal springs (Tshipise, Sagole and Mphephu) was carried out (Tekere et al, 2012). The study revealed that the springs contained elements such as sodium (156.31 mg L^{-1}, 65.15 mg L^{-1}, 44.37 mg L^{-1} respectively), potassium (4.25 mg L^{-1}, 1.10 mg L^{-1}, 1.14 mg L^{-1}), calcium (5.58 mg L^{-1}, 1.31 mg L^{-1}, 13.73 mg L^{-1}) and magnesium (0.17 mg L^{-1}, 0.07 mg L^{-1}, 11.25 mg L^{-1}) including trace amounts of elements such as arsenic (0.14 µg L^{-1}, 2.88 µg L^{-1}, 0.43 µg L^{-1}), cadmium (0.02 µg L^{-1}, 0.01 µg L^{-1}, 0 µg L^{-1}) chromium (0.70 µg L^{-1}, 0.49 µg L^{-1}, 1.20 µg L^{-1}), lead (0.08 µg L^{-1}, 0.12 µg L^{-1}, 0.16 µg L^{-1}) and mercury (0.33 µg L^{-1}, 0 µg L^{-1}, 0.23 µg L^{-1}). Magnabosco et al. (2014) carried out a study on six thermal springs in the Limpopo Province: Eiland, Mphephu, Sagole, Souting, Siloam and Tshipise. The study showed the presence of sodium, potassium, calcium, magnesium, nitrate, chloride and sulphate. The concentrations of these chemical species in all six thermal springs ranged from as low as 2.9×10^{-6} M (magnesium in Sagole) to as high as 1.6×10^{-1} M (chloride in Souting).

2.12 Instrumentation

2.12.1 Inductively coupled plasma mass spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful tool for analysing trace metals in environmental samples (Bazilio and Weinrich, 2012). Figure 2.5 shows the periodic table of the elements. The elements shaded in yellow can be analysed by ICP-MS whereas the elements shaded in red cannot. The figure shows that ICP-MS can analyse most elements in the periodic table, including elements that are common pollutants of water such as heavy metals. This makes ICP-MS an important analytical technique with regards to environmental monitoring. The figure also indicates that inductively coupled plasma mass spectrometry is a highly sensitive experimental technique, capable of detecting analytes in environmental samples with detection limits as low as µg L^{-1}. This is crucial for effective trace analysis of analytes in samples. The pink and blue values below each element symbol reflect empirical concentrations obtained by quadrupole and high-resolution ICP-MS respectively. Quadrupole ICP-MS is principally used for rapid, precise and accurate trace element determinations (often at sub ng L^{-1} concentrations) in liquid and solid samples (University of Texas at Austin, 2018). The researchers at the Jackson School of Geosciences at the University of Texas at Austin also noted that a quadrupole consists of four parallel rods, often made of gold-coated ceramic or molybdenum, that filter out non-analyte, matrix and interfering ions, allowing only desired analyte ions of a single mass-to-charge ratio to be transmitted to the detector. This allows for a more accurate analysis of samples.

The USGS (2013) acknowledges that, although quadrupole ICP-MS is sensitive enough for many routine applications, there are however some instances when its resolution is not sufficient enough to separate overlapping molecular or isobaric interferences from the elemental isotope of interest. This is where high resolution ICP-MS comes into play. Although this technique allows the analyst to eliminate or reduce the effect of interferences due to mass overlap, its drawback is reduced sensitivity, which can limit detection capabilities where the analyte concentrations are very low (USGS, 2013).



Limits of detection in parts per billion (ng/ml)

Quadrupole ICP-MS
High-Resolution ICP-MS

Values reflect actual experimental data gathered over more than 1 year and are calculated from 3 sigma of an aqueous blank.

Not measured by ICP-MS

H																	He
Li 0.4 0.002	Be 0.04 0.003											B 0.5 0.28	C	N	O	F	Ne
Na 0.4 1.1	Mg 0.06 0.07											Al 0.02 0.2	Si N/A 0.6	P N/A 0.5	S N/A 1.1	Cl N/A 159	Ar
K N/A 0.15	Ca N/A 0.3	Sc 0.2 4E-04	Ti 1.3 0.04	V 0.001 0.001	Cr 0.2 0.004	Mn 0.01 0.03	Fe N/A 0.05	Co 9E-04 0.005	Ni 0.2 0.08	Cu 0.01 0.03	Zn 0.02 0.04	Ga 0.001 0.002	Ge 0.01 0.009	As 0.1 0.02	Se 0.3 0.01	Br	Kr
Rb 0.003 0.007	Sr 4E-04 0.005	Y 1E-04 1E-04	Zr 0.001 0.001	Nb 2E-04 1E-09	Mo 7E-04 0.006	Tc	Ru 0.001 1E-04	Rh 1E-04 0.003	Pd 0.001 1E-04	Ag 9E-04 0.003	Cd 0.003 0.002	In 3E-04 5E-04	Sn 0.002 0.008	Sb 6E-04 6E-04	Te 0.009 1E-04	I	Xe
Cs 0.001 1E-04	Ba 0.002 0.002	La 1E-04 1E-04	Hf 5E-04 1E-04	Ta 2E-04 3E-05	W 7E-04 0.001	Re 2E-04 0.001	Os 3E-04 0.001	Ir 2E-04 0.001	Pt 5E-04 1E-05	Au 0.002 3.1	Hg 0.6 0.06	Tl 2E-04 1E-04	Pb 0.001 0.009	Bi 3E-04 5E-04	Po	At	Rn
Fr	Ra	Ac															
			Ce 2E-04 0.001	Pr 2E-04 1E-04	Nd 4E-04 2E-04	Pm	Sm 5E-04 1E-04	Eu 2E-04 2E-05	Gd 9E-04 1E-04	Tb 1E-04 1E-05	Dy 3E-04 1E-04	Ho 2E-04 1E-04	Er 3E-04 1E-04	Tm 1E-04 1E-04	Yb 4E-04 2E-05	Lu 2E-04 1E-05	
			Th 1E-04 2E-05	Pa	U 2E-04 3E-04	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Figure 2.5 Elements whose concentration can be measured by ICP-MS (Elemental Analysis Incorporated, 2016).

Inductively coupled plasma mass spectrometry is increasingly becoming a favoured analytical technique for trace analysis due to the following reasons; the instrument detection limits are at or below the single part per trillion (ng L^{-1}) level for much of the periodic table, the analytical working range is >10 orders of magnitude, its productivity is unsurpassed by any other technique and isotopic analysis can be achieved readily (Perkinelmer, 2017).

Figure 2.6 shows a schematic drawing of the ICP-MS. The liquid sample is introduced into the instrument via a peristaltic pump where it encounters a nebulizer. The nebulizer converts the liquid sample into a fine spray comprising of both small and large droplets, a process known as nebulisation. The larger droplets drain away as waste whilst the smaller droplets are injected into an argon plasma that is at a temperature of approximately 5730°C. The liquid spray is then vaporised, atomised and ionised then injected into a mass spectrometer which then detects the various elements present in the sample. The mass spectrometer is electronically linked to a monitor which then displays the results of the analysis.

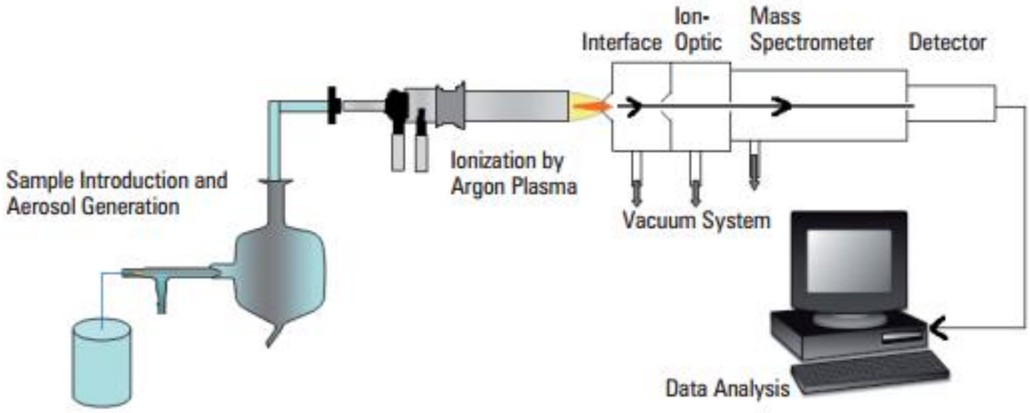


Figure 2.6 Schematic diagram for ICP-MS (Spectro Ametek materials analysis division, 2018).

Table 2.5 shows some common instrument detection limits of some select elements as reported by the University of Manchester. The detection limits, which are in ng L^{-1}, show the sensitivity of ICP-MS. Some elements can even be detected down to the part per quadrillion level (University of Manchester, 2016). Most pollutants in the environment, particularly heavy metals, occur in trace concentrations and require very sensitive instrumental techniques in order to be detected. This is why ICP-MS is a key analytical technique as far as environmental monitoring is concerned.

Table 2.5 Common ICP-MS detection limits for some select elements.

Elements	Instrument detection limit (ng L^{-1})
U, Cs, Bi	<10
Ag, Be, Cd, Rb, Sn, Sb, Au	10-50
Ba, Pb, Se, Sr, Co, W, Mo, Mg	50-100
Cr, Cu, Mn	100-200
Zn, As, Ti	400-500

2.12.2 X-ray fluorescence

X-ray fluorescence (XRF) is used for the analysis of the chemical composition of both solids and liquids (Brouwer, 2003). Brouwer also noted that XRF can be used to determine the thickness and composition of layers and coatings of various materials in a fast, accurate and non-destructive manner.

A small amount of sample, in this case a dried soil sample, is introduced by a thin tube onto boric acid which is used as a binder, to keep the sample in place. The mixture is then compressed into a circular pellet of just a few millimetres in thickness. The pellet is then inserted into the instrument upside down and bombarded with X-rays. The X-rays knock off lower energy electrons in atoms of the material. Higher energy electrons then lose energy as they descend to lower energy levels to replace the lost electrons. As they descend, they release characteristic radiation which is then detected by the instrument. This characteristic radiation reveals not just the identity of the element but its concentration in the sample. Figure 2.7 shows the Bruker axs S2 ranger XRF instrument used to analyse the soil samples from the three thermal springs. On the far left of the figure is the instrument itself, with a little touch screen monitor for setting up the parameters of the analysis before the analysis begins. Above the touch screen monitor is a light that turns orange when the x-rays are on. To the right of the touch screen monitor, on the flat top part of the instrument, is a circular hole/port in which the pellet is placed for analysis. The port opens and closes automatically before analysis begins. On the wooden table itself, in plastic petri dishes, are the pellets whose chemical composition was determined. To the right of the figure is the desktop monitor where all the results are viewed and collected after analysis.

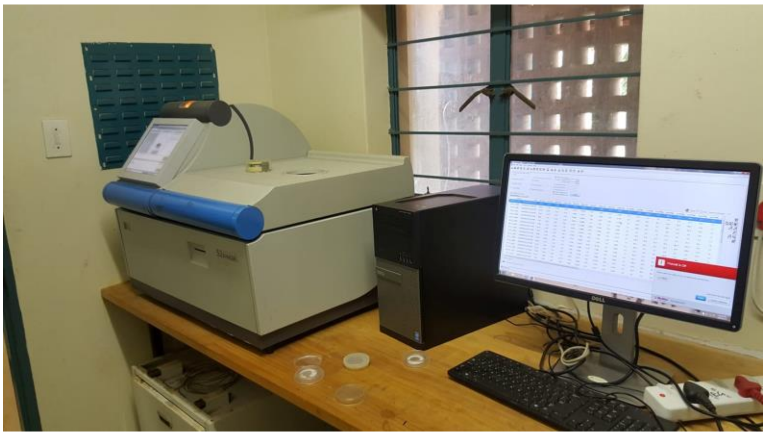


Figure 2.7 Brucker axs S2 Ranger XRF instrument (This work, 2018).

Figure 2.8 shows a schematic diagram of how an XRF instrument works. The X-ray tube fires a beam of x-rays at the sample pellet. The sample pellet is placed upside down with the actual sample facing downwards towards the incoming x-ray beam. The sample is placed in a vacuum to prevent any particulates that may be present in air from contaminating the sample. This safeguards the integrity of the results obtained from the analysis. After the sample is bombarded by the incoming x-ray beam, the sample releases characteristic radiation which is then detected by the detector. The detector is cooled so as to avoid it over-heating during bombardment with characteristic radiation released from the sample during analysis. The detector is also electronically linked to a computer which then displays the results of the analysis as interpreted by the detector.

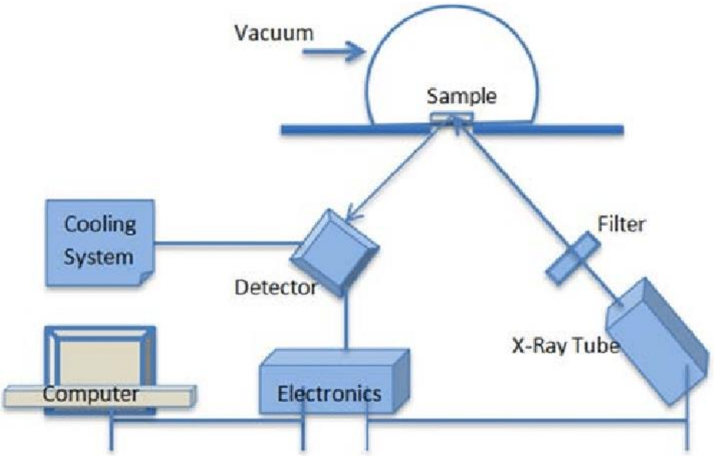


Figure 2.8 Typical schematic diagram for XRF instrumentation (Chaqmaqchee et al. (2017).

CHAPTER THREE: METHODOLOGY

3.1 Study area

Tshipise thermal spring is located on the grounds of a well-developed tourist resort. The resort has many huts and other accommodation for tourists. The thermal spring itself is located at the base of a hill and is surrounded by lush green vegetation. The soil in which this vegetation grows is rich in organic matter. The mouth of the thermal spring is surrounded by a fence so that tourists can view the spring without running the risk of falling over into the reservoir which is several meters deep. The mouth of the spring is also covered by algae. The Global Positioning System (GPS) coordinates for Tshipise thermal spring are 22° 53’ 08.65” S and 30° 12’ 41.38” E.

Mphephu is a thermal spring also located within a well-developed tourist resort. The spring is much smaller than the Tshipise thermal spring and is also very shallow, about 30 cm at its deepest. Like the Tshipise thermal spring, the Mphephu thermal spring reservoir has had stone masonry built around it however not as extensively as the Tshipise thermal spring reservoir. The Mphephu thermal spring is surrounded by loose sandy soil, devoid of any vegetation except large trees that grow around the thermal spring reservoir and have overhanging branches over the spring. Mphephu thermal spring is also at the foot of a hill. The hill is also covered in loose, sandy soil and is devoid of any significant amount of vegetation. The GPS coordinates for Mphephu thermal spring are 22° 40’ 03.54” S and 22° 54’ 02.65” E.

Siloam borehole is located on the grounds of a private household. The mineral water from the borehole is used for many domestic purposes such as washing clothes, dishes and bathing. It acts as a vital source of water in an otherwise water deprived area. The GPS coordinates for Siloam borehole are 22° 34’ 06.46” S and 30° 12’ 23.02” E.

Figure 3.1 below shows a map of the sampling area. The map shows the location of Tshipise thermal spring, Mphephu thermal spring and Siloam borehole. As shown in the figure, the thermal springs are situated in the northern part of the Limpopo Province. The figure also shows that Mphephu thermal spring and Siloam borehole are quite close to each other. In fact, the two sampling sites are separated by less than 1 km.

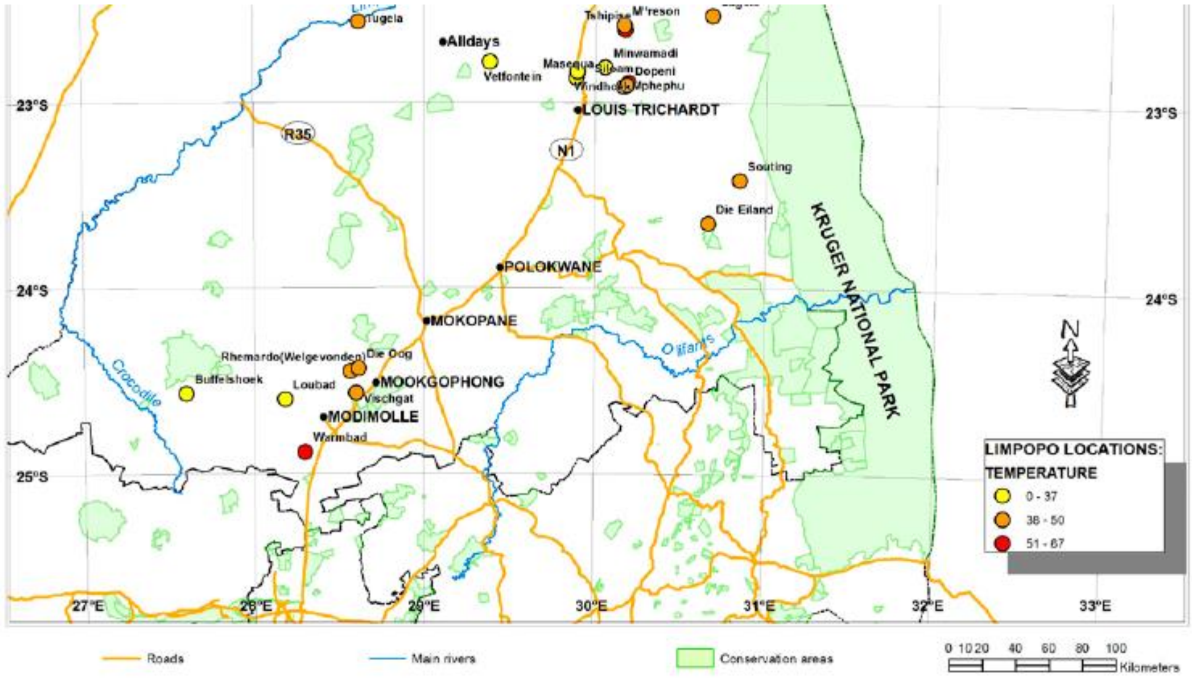


Figure 3.1 Map detailing the location of Tshipise thermal spring, Mphephu thermal spring and Siloam borehole.

3.2 Sampling methods

3.2.1 Water sample collection, storage and preparation

Water samples were collected from Tshipise thermal spring, Mphephu thermal spring and Siloam borehole once per week every week for the month of February in 2018. Sterile plastic sampling bottles (500 mL) were used to collect the samples. A few drops of a 1 mol L^{-1} HNO_3 solution were added to the sampling bottles. This was done to prevent any heavy metals present in the water samples from precipitating out of solution during storage. The water samples were stored in a refrigerator at a temperature just above freezing until analysis. Before analysis, the sampling bottles were thoroughly shaken to dislodge any metals that may have adsorbed onto the inner surface of the sampling bottles.

3.2.2 Soil sample collection and preparation

Soil samples were collected from multiple spots next to the three sampling sites. The soil samples were put in labelled brown bags and dried at low heat in oven overnight. This step was particularly important because sometimes the soil was wet from the rains in the area before or at the time of sampling.

Small pieces of quartz were broken off from a large quartz rock (using a sledge hammer) and thrown into a crusher where they were broken down into tiny little pieces. The tiny pieces of quartz were used for cleaning the milling pot. A milling pot is used to mill the dry soil sample into a fine powder before XRF analysis. Cleaning the milling pot is essential to avoid contamination of new samples by left over material from previous samples. The tiny pieces of quartz have jagged edges that are abrasive. This abrasiveness is what scours the insides of the milling pot, cleaning it in the process.

Once the milling pot was clean, the dry soil samples were milled into a fine powder using a Retsch RS 200 milling machine (Mammelzen, Germany) until they had the consistency of a fine powder and then made into a pellet using pellet making tools and a compressor. The compressor was used to compress the boric acid powder from Rochelle chemicals and laboratory equipment (Johannesburg, South Africa) and soil sample at 30 tons of pressure into a solid pellet ready for XRF analysis. The pellet was then placed onto a pellet holder upside down, that is, the soil sample facing the bottom of the XRF instrument and bombarded with x-rays. The results of the analysis were displayed on a monitor, collected and tabulated. The above procedure was repeated for the other two soil samples.

3.3 Analytical methods

3.3.1 Water sample analysis

The analysis of the water samples began on site, when the water samples were collected and analysed for their physico-chemical properties. A portable pH meter with the ability to also measure temperature, Total dissolved solids (TDS) and electrical conductivity (EC) was used. In the laboratory, the ICP-MS was then used to measure the concentration of the various metals present in the water samples.

An ICP-MS from Perkinelmer (Midrand, South Africa), was used for the determination of the chemical composition of the water samples with parameters shown in Table 3.1. Before analysis, all glass ware needed to make the relevant standard solutions was thoroughly cleaned. The chemicals used for the ICP-MS analysis were also ultra-pure, given their assays. The de-ionised water used for rinsing was also replaced with fresh de-ionised water. The sampling passing route in the instrument was also thoroughly cleaned to prevent any contamination of the sample with residues from previous analyses. The mineral water samples were also filtered using a 0.45 µm filter paper to filter out any solid particulates that would have clogged and damaged the instrument during analysis. After filtration, in each case, the filtrate was acidified with a few drops of a 10% (v/v) HNO_3 solution. After all these preparatory steps were concluded, the standard solutions were run to generate a calibration graph which was then used to quantify the elements in the mineral water samples.

Table 3.1 Essential operating conditions of the ICP-MS.

Parameter	Setting
Auxiliary Gas Flow (L min^{-1})	1.2
Measurement Time (s)	90
Nebulizer	PFA ST
Nebulizer Gas Flow (L min^{-1})	0.98
Plasma Gas Flow (L min^{-1})	16.00
Replicates per sample	3
RF Power (W)	1600
Sample Uptake rate (µL min^{-1})	270
Spray Chamber	Peltier-cooled baffled quartz cyclonic
Triple Cone Interface Material	Nickel

3.3.2 Soil sample analysis

An S2 Ranger XRF instrument from Bruker axs (Pty) Ltd, (Massachusetts, USA) was used for the determination of the chemical composition of the soil samples collected from the immediate vicinity of the two thermal springs and borehole.

Before analysis, a reference material with known mineral composition was used to calibrate the XRF instrument. The reference material used contained many elements and metal oxides whose exact quantities were known. After running the reference material, the values obtained were compared to the known composition of each element and metal oxide in the reference material. The closer the two values were, the better. This was an indication that the instrument was well calibrated. After calibrating the instrument, the soil samples were then analysed for their mineral composition.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Quality control data

Quality control data is essential to create a high degree of trust in any data reported by an analyst. See quality control data for water sample analyses in Appendix B labelled QC1 and QC2 respectively. In addition, all quality control data for soil sample analyses is in Appendix C.

4.2 Water sample data

4.2.1 Physico-chemical properties of water

The water samples from Tshipise thermal spring, Mphephu thermal spring and Siloam borehole had four physico-chemical properties measured: Total dissolved solids (TDS), pH, temperature and electrical conductivity (EC). Table 4.1 shows these physico-chemical properties.

Table 4.1 Physico-chemical properties of water samples.

Thermal spring	TDS (mg L^{-1})	pH	Temperature (°C)	EC (µS cm^{-1})
Tshipise	405	8.67	64	675
Mphephu	198	7.40	43	330
Siloam	439	7.25	38	730

Mphephu thermal spring and Siloam borehole can be described as having a pH that is almost neutral whilst Tshipise mineral water is mildly alkaline. Tshipise mineral water is scalding at 64°C whilst Mphephu and Siloam mineral water are warm, having temperatures of 43°C and 38°C respectively. Tshipise and Siloam have the highest TDS, which is a measure of dissolved inorganic and organic components in the water. Tshipise thermal spring and Siloam borehole also have the highest EC.

Table 4.1 shows a direct proportionality between TDS and EC. As TDS values increase from 198 mg L^{-1} to 439 mg L^{-1}, EC also increases from 330 µS cm^{-1} to 730 µS cm^{-1}. Electrical conductivity is the ability of water to carry an electrical current. Moore et al. (2008) defined EC as a measure of the ease with which electrical current can pass through water. The same proponents of the study further noted that the EC of aqueous solutions depends on the presence of charged ions in the solution. However, as the concentration of ions increases, EC can also decrease as the interactions among the ions can impede their mobility. Electrical conductivity is a useful indicator of TDS because the conduction of current in an electrolyte solution is primarily dependent on the concentration of ionic species in the electrolyte solution (Hayashi, 2004). Furthermore, Hayashi (2004) stated that EC is widely used for monitoring the mixing of fresh and saline water, separating stream hydrographs and geophysical mapping of contaminated groundwater.

The TDS parameter is a key measurement of mainly dissolved inorganic material in water. Therefore, the higher the TDS, the greater the concentration of dissolved ions in the water, the greater the EC. According to Oram (2014), TDS comprise inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulphates) and some small amounts of organic matter dissolved in water. A WHO (1996) report stated that TDS are inorganic salts and small amounts of organic matter present in solution.

The 1996 WHO report also noted that some potential sources for TDS in water are either natural or man-made. Natural sources can include rocks and soil. Man-made sources include; Sewage, urban runoff, agricultural runoff and industrial wastewater. Oram (2014) stated that potential sources of TDS include; Sewage, urban runoff, industrial wastewater, agricultural runoff, water treatment chemicals, the nature of the piping used to convey water, sea water intrusion (affecting coastal regions) and salts used for road de-icing (in northern latitudes with snow). The areas immediately surrounding Tshipise thermal spring, Mphephu thermal spring and Siloam borehole are primarily rural and agricultural in nature. Therefore, possible sources of TDS include agricultural runoff and sewage due to lack of proper sanitation in many households. Tshipise and Mphephu are open reservoirs exposed to wildlife, particularly baboons that are abundant in the area. It is conceivable that dung from such animals can find its way into the thermal springs (directly or indirectly through surface runoff), contributing to the TDS values recorded in the water samples collected from these two springs.

Many studies have been carried out on the thermal springs in Limpopo Province. Each study has produced its own set of results on the physico-chemical properties of the various mineral waters. Jonker et al. (2013) and Nyabeze et al. (2013) both carried out a study on Mphephu thermal spring, Siloam borehole and Tshipise thermal spring. The temperatures recorded for the two studies were 43°C, 67.5°C, 58°C and 44°C, 66°C, 58°C respectively. Nyabeze et al. (2013) recorded an almost similar temperature for Mphephu as that shown in Table 4.1. The Tshipise temperature, although at 58°C, is not too different from that shown in Table 4.1 in the sense that both temperatures indicate the mineral water from Tshipise thermal spring is scalding. The Siloam temperature recorded by Nyabeze et al. (2013) (66°C) is vastly different from that shown in Table 4.1 (38°C). This is most likely due to a difference in sampling sites. The Siloam site where Nyabeze et al. (2013) sampled has most likely long since dried up, according to members of the community. At 67.5°C, the temperature recorded by Jonker et al. (2013) for Siloam is scalding whereas Table 4.1 shows that the temperature of Siloam mineral water is warm at 38°C. This is probably because this author may have sampled at a different site which may long since have dried up leaving only the borehole site (Figure 2.3) as the only viable sampling site for Siloam mineral water. When asked, community members did state that the main source for Siloam mineral water had dried up roughly 2 years ago. Jonker et al. (2013) recorded TDS and pH values of (199.36 mg L^{-1}, 197.3 mg L^{-1} and 460.56 mg L^{-1}) and (8.08, 9.51 and 8.85) respectively for all three sites. Jonker et al. (2013) also measured the EC of the water samples and recorded them as 440 µS cm^{-1}, 390 µS cm^{-1} and 810 µS cm^{-1} respectively. The difference between Jonker's TDS values and those shown in Table 4.1 may be due to the gradual change in the dissolved ion composition of the mineral water as the spring ages. Another reason for the difference could be that Jonker sampled the mineral water after a particularly heavy rainy season. Heavy rains would have washed, through surface runoff, any inorganic minerals in the surrounding soil into the reservoir of the spring thus increasing the TDS value. The Siloam TDS values are vastly different probably due to a difference in sampling sites.

Olivier et al. (2004) studied Tshipise and Mphephu mineral waters and recorded temperatures of 58°C and 43°C respectively. Olivier et al. (2010) measured the temperature of Tshipise and Mphephu thermal springs and found the temperatures unchanged. The temperatures had remained unchanged in the six-year period that had elapsed between the two studies. The temperature recorded for Mphephu thermal springs in this study is the same as that recorded by the two studies outlined above. Although the recorded temperature for Tshipise thermal spring in this study is higher (Table 4.1) than that recorded by Olivier et al. (2004) and Olivier et al. (2010), both temperatures indicate the scalding nature of water from Tshipise thermal spring.

Recordings of the pH for Tshipise and Mphephu water samples were also done on site and found to be 8.70, 8.24 and 8.94, 8.19 for Olivier et al. (2004) and Olivier et al. (2010) respectively. The pH value for Tshipise in this study (Table 4.1) is between 8 and 9 like the two studies compared, indicating a mildly alkaline pH as well. Although the Mphephu mineral water pH for this study (Table 4.1) is consistently lower than the pH values recorded for Mphephu mineral water by Olivier et al. (2004) and Olivier et al. (2010), all pH values indicate mild alkalinity of the Mphephu mineral water samples.

There is no significant difference between the Mphephu TDS of this work (2018) (Table 4.1) and the TDS value for Mphephu recorded by Olivier et al. (2010) at 199.36 mg L^{-1}. However, there is a notable difference between the Mphephu TDS value recorded by Olivier et al. (2004) at 175.90 mg L^{-1} and that recorded in Table 4.1. Perhaps the sampling in 2004 took place during a much drier period than the samplings in 2010 and 2018. In fact, during sampling for this work (2018), the soils immediately around the Mphephu thermal spring were damp indicating recent rains in the area. The rains may have washed some inorganic materials into the thermal spring through surface runoff, raising TDS values just before sampling took place. Total dissolved solids for Tshipise mineral water were found to be 422.10 mg L^{-1} by Olivier et al. (2004). The TDS value for Tshipise in this study (Table 4.1) is lower than that recorded by Olivier et al. (2004), though not by much. Tshipise is a much more closed system than Mphephu, the reservoir having undergone significant construction around it to protect it from the elements. Therefore, unlike Mphephu, the Tshipise reservoir is unlikely to be affected by surface runoff to the same extent as the Mphephu thermal spring. This is probably why the difference between the Tshipise TDS values for Olivier et al. (2004) and this work (2018) is small, a difference of 17.1 mg L^{-1}, compared to the 22.1 mg L^{-1} difference between the Mphephu TDS values for Olivier et al. (2004) and this work (2018).

A comparison of the Siloam borehole physico-chemical parameters in Table 4.1 and those recorded by Tekere et al. (2011) reveals significant differences. Tekere et al. (2011) recorded a temperature of 63°C, a pH value of 9.5, a TDS value of 197.32 mg L^{-1} and an EC value of 390 µS cm^{-1}. The stark differences are probably because Tekere et al. (2011) sampled at a different source that, according to the local inhabitants of the area, dried up roughly two years ago (2016).

Table 4.2 shows the temperature classifications of mineral water samples from Mphephu, Tshipise and Siloam. The table compares temperature classifications used in this work (2018) and those found in literature for the same thermal springs. Olivier et al. (2004), Olivier et al. (2010), Jonker et al. (2013) and Nyabeze et al. (2013) are all in agreement with their temperature classification of the mineral water from Tshipise thermal spring, Mphephu thermal spring and Siloam borehole. This work (2018) is in agreement with the other four studies as far as the temperature classification for Tshipise thermal spring is concerned. However, this work (2018) classifies both Mphephu and Siloam mineral water as warm.

Table 4.2 Temperature classification of Tshipise thermal spring, Mphephu thermal spring and Siloam borehole.

Thermal spring	Olivier et al. (2004)	Olivier et al. (2010)	Jonker et al. (2013)	Nyabeze et al. (2013)	This work (2018)
Tshipise	Scalding	Scalding	Scalding	Scalding	Scalding
Mphephu	Hot	Hot	Hot	Hot	Warm
Siloam	Scalding	Scalding	Scalding	Scalding	Warm

Although all four studies agree with the temperature classification of Tshipise thermal spring, there is significant disagreement on the other two thermal springs (Mphephu and Siloam). The table shows that Tshipise mineral water has not changed much in 8 years as far as the scalding nature of the mineral water is concerned. The other four studies, two of them carried out in 2013, classify Mphephu and Siloam mineral water as hot and scalding respectively.

The two studies carried out in 2013 have the same temperature classifications for all three thermal springs probably because the studies were done in the same year. The 2010 study also has the same temperature classification as the two 2013 studies probably because it was done not so long ago relative to the 2013 studies, just two years prior. However, a lot can change in seven years as the elements take their tole and thermal springs age. The 2018 study shows that the mineral water from Mphephu and Siloam has cooled significantly in the 8 years since the 2010 study. When sampling was carried out at Mphephu thermal spring in February 2018, an entire hand could be submerged for an indefinite period of time without any discomfort. The water was warm, not hot. The same was observed when obtaining samples from the Siloam thermal spring borehole.

The Mphephu resort put up a sign next to the spring describing the mineral water (Figure 4.1). Although the sign describes the water as hot, the water is warm. A hand can be fully submerged in the water indefinitely without being scalded or feeling any discomfort whatsoever.

Figure 4.1 Sign describing Mphephu mineral water.

Figure 4.2 shows the concentration comparison of Ca and Mg in the Tshipise thermal spring, Mphephu thermal spring and Siloam borehole water samples respectively. The figure shows that Siloam has the highest concentration of Mg at 121.13 mg L^{-1} with Tshipise having the least Mg concentration at 4.67 mg L^{-1}. The figure also shows that the same pattern is observed with regards to the concentration of Ca. Siloam has the highest concentration of Ca at 28.71 mg L^{-1} with Tshipise having the least Ca concentration at 8.25 mg L^{-1}.

Studies prior to this one have also determined the water hardness of Tshipise thermal spring, Mphephu thermal spring and Siloam borehole. Olivier (2004) carried out an analysis of water samples from Tshipise and Mphephu thermal springs and reported Ca and Mg concentrations of 2.84 mg L^{-1}; 0.01 mg L^{-1} and 13.35 mg L^{-1}; 10.60 mg L^{-1} respectively. The Tshipise Ca and Mg concentrations shown in Figure 4.2 are both much higher than those reported by Olivier (2004). This may be because Olivier (2004) may have sampled the mineral water after particularly heavy rainfall in the area. These heavy rains would have had the effect of diluting the mineral water significantly as Tshipise is an open top reservoir exposed to the elements. However, comparing the Mphephu thermal spring Ca and Mg data in Figure 4.2 with that obtained by Olivier (2004) shows that the Ca concentration for this work (2018) is approximately twice as high as that recorded by Olivier (2004). The Mg concentration for this work (2018) is more than ten times the concentration of Mg recorded by Olivier (2004). This difference may again be down to several factors such as; A difference in sampling occasions, the use of different instrumentation in analysing the water samples and perhaps a difference in laboratory conditions during the actual analysis of the water samples.

Olivier et al. (2010) recorded a Ca and Mg concentration for Tshipise thermal spring, Mphephu thermal spring and Siloam borehole of 5.58 mg L^{-1}; 0.17 mg L^{-1}, 13.73 mg L^{-1}; 11.25 mg L^{-1} and 1.40 mg L^{-1}; 0.08-1.30 mg L^{-1} respectively. Both Ca and Mg concentrations for Tshipise and Mphephu thermal springs increased slightly in the six-year period between the 2004 and 2010 studies. Compared to the water hardness concentrations obtained six years earlier in 2004, the Ca and Mg concentrations obtained by Olivier et al. (2010) for Tshipise and Mphephu show no great variation, largely remaining similar in magnitude. The difference between the 2010 results for Tshipise and Mphephu thermal springs and the concentrations obtained by this work (2018) are very similar to the differences between the Ca and Mg concentrations obtained by Olivier (2004) and those recorded by this work (2018). The Siloam Ca and

Mg concentrations recorded by Olivier et al. (2010) are vastly lower than those in Figure 4.2. Environmental factors such as rainfall and by extension dilution of the mineral water could well have played a role in such a discrepancy between the values. In fact, during the 2010-2011 rainy season, Southern Africa was characterised by extremely heavy rainfall leading to the South African Government declaring several disaster zones (The Guardian, 2011). Since then, probably due to climate change effects, rainfall has been erratic and this could have resulted in the concentration of Ca and Mg in the mineral water, leading to the very high concentrations recorded by this work (2018). In addition, Olivier et al. (2010) may have sampled at a source that has long since run dry. When asked, the local residents did admit that one of the sources for Siloam mineral water had long since dried up.

Durowoju et al. (2016) ascertained the Ca and Mg concentration in water samples from Siloam borehole and Tshipise thermal spring. The study showed the Ca and Mg concentrations in Siloam borehole and Tshipise thermal spring to be 5.65 mg L^{-1}; 1.09 mg L^{-1} and 8.12 mg L^{-1}; 1.17 mg L^{-1} respectively. A comparison with water hardness concentrations in Figure 4.2 shows that the Tshipise Ca concentration recorded by Durowoju et al. (2016) is approximately the same as that recorded by this work (2018). In general, there is an increase in the Ca and Mg concentrations in both Tshipise thermal spring and Siloam borehole from the year 2010 to 2018. South Africa has grappling with a severe drought (BBC news, 2015) for several years now and this may have served to concentrate the minerals Ca and Mg in the thermal springs leading to higher concentrations detected as the years went by.

A study of the chemical composition of water samples drawn from Siloam borehole by Tekere et al. (2011) revealed the presence of Ca (1.38 mg L^{-1}) and Mg (13.33 mg L^{-1}). The comparison of these values with the Ca and Mg concentrations for Siloam shown in Figure 4.2 shows a vast difference once again which could be down to any of the aforementioned reasons.

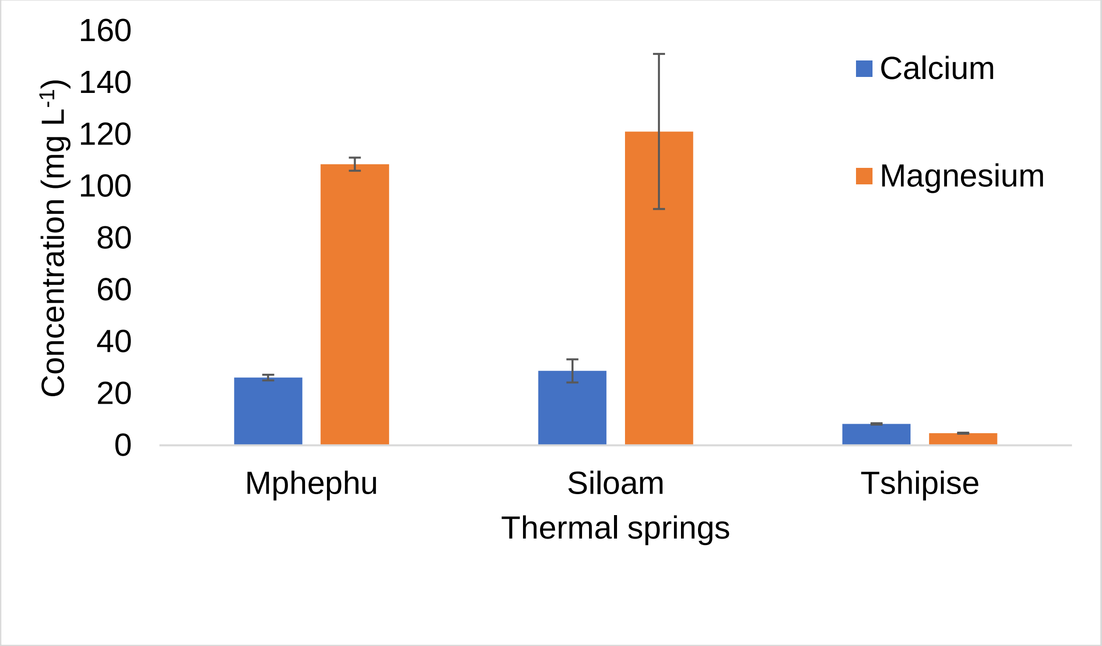


Figure 4.1 Water hardness comparison for the three sampling sites.

Table 4.3 shows the water hardness criteria for Ca and Mg adopted by this work (2018) based on water hardness criteria used by the USGS and WQA (Table 2.3). Table 4.3 shows that according to both the recorded Ca and Mg concentrations by this work (2018), Tshipise mineral water is soft. Mphephu mineral water would be considered soft or moderately hard according to Ca and Mg concentrations respectively. Looking at only the Mg concentration, Siloam mineral water would be considered hard.

Table 4.3 Water hardness criteria adopted by this work (2018) based on USGS and WQA criteria.

Reference	Tshipise		Mphephu		Siloam	
	Ca	Mg	Ca	Mg	Ca	Mg
This work (2018)	S	S	S	MH	S	H

*S (Soft); MH (Moderately Hard); H (Hard)

4.2.2 Heavy metal analysis of water samples

Figure 4.3 shows a comparison of the concentrations of five select elements (As, Cd, Cr, Cu and Ga) in the water samples from Tshipise, Mphephu and Siloam thermal springs (see other elements in appendix B). The figure shows that Siloam has the highest total Cr concentration (62.90 µg L^{-1}) of all three thermal springs. Siloam thermal spring also has the highest As concentration of all three thermal springs at 20.97 µg L^{-1} whereas Mphephu thermal spring has the highest Cd concentration at 8.47 µg L^{-}1. According to Table 2.1, the As concentration in all three thermal springs exceeds the MAC which has been set by the WHO at 10 µg L^{-1}. This is a cause for concern as As is known for its negative health effects (Section 2.10). As can be introduced into both surface and sub-surface water reservoirs by either man-made activities or through natural leaching of minerals from surrounding rock strata. Since the sampling sites where largely rural with no heavy mining or industrial activities nearby, the presence of As in the mineral water is most likely as a result of leaching of rocks.

Although the Cd concentration is below the MAC set by the WQA (Table 2.1) for both Siloam and Tshipise mineral water (3.73 µg L^{-1} and 4.63 µg L^{-1} respectively), it is nonetheless concerning as both are close to the set MAC and because heavy metals are known to accumulate in the body over a period, building up their concentrations gradually until they reach toxic levels (Singh et al. 2011). The Mphephu mineral water sample exceeded the MAC set by the WQA (2018).

No speciation of Cr was carried out in this work (2018). Only total Cr was measured. There are various oxidation states of Cr but the most studied are Cr (III) and Cr (VI) of which Cr (VI) is toxic and makes up about 35% of all Cr released from anthropogenic activities such as chromium plating, chemical manufacturing of Cr and evaporative cooling towers (Guertin, 2004). None of these industries exist in the largely rural area from where the samples were obtained. It would therefore be reasonable to assume (subject to confirmation by further research) that the Cr present in the samples is unlikely to be Cr (VI). The MAC set for Cr (VI) by the United States based National Institute for Occupational Health and Safety is 0.001 µg L^{-1}. This is an indication of the toxicity of Cr (VI).

Olivier et al. (2011) found the presence of Cr in Mphephu and Siloam at the concentrations of 1.2 µg L^{-1} and 0.97 µg L^{-1} respectively. The Cr concentration for Mphephu and Siloam recorded by this study (39.90 µg L^{-1} and 62.90 µg L^{-1} respectively) are much higher than those recorded in the 2011 study. With regards to Siloam, this may be due to a difference in sampling sites as mentioned before. The difference in the Cr concentrations for Mphephu thermal spring may be down to environmental factors (rain and evaporation) or even a difference in the seasons in which the samples were obtained.

Tekere et al. (2011) analysed water drawn from Siloam thermal spring for heavy metals and found the Cd concentration to be below the detection limit of the instrumentation that was being used. The difference between Tekere et al. (2011) and this work (2018) with regards to the Cd concentration could be two-fold; A difference in sampling site or a much less sensitive instrument may have been used in the 2011 study to analyse the water samples.

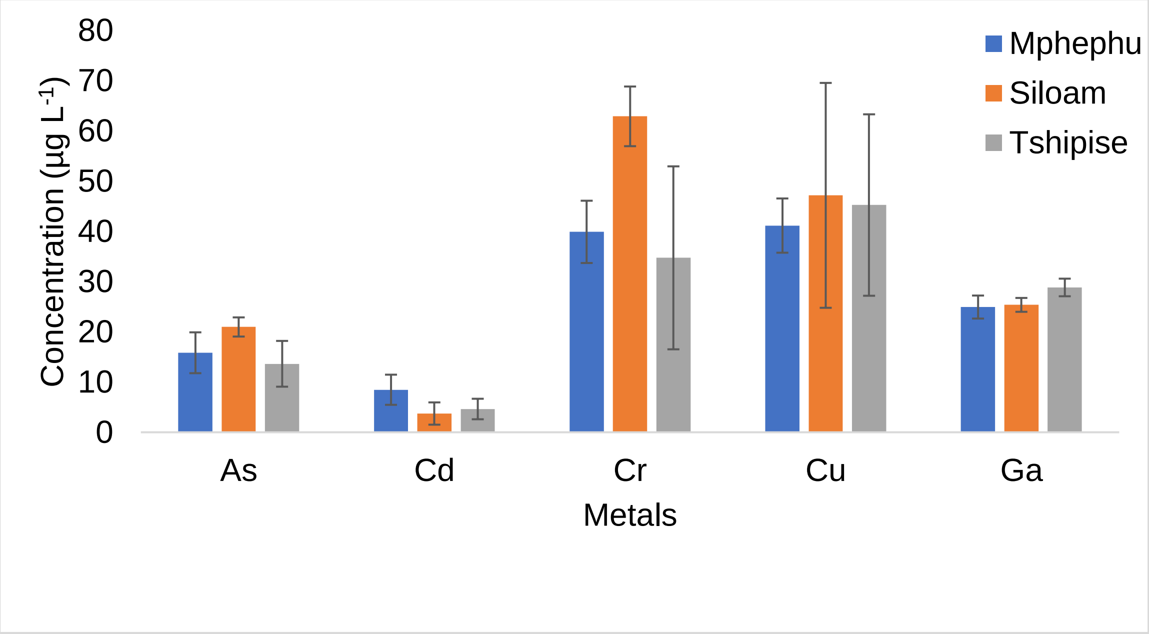


Figure 4.2 Heavy metal comparison of select heavy metals for the three sampling sites.

4.3 Soil sample data

4.3.1 Major oxide analysis

Table 4.4 shows a comparison of the major oxides present in the three soil samples collected from the immediate vicinity of Tshipise thermal spring, Mphephu thermal spring and Siloam borehole. The table shows the mass percentage composition that each oxide makes up in the sample. SiO_2 makes up the bulk of the composition of all three soil samples indicating the sandy nature of the soils, especially Mphephu. The oxides making up the least composition of all three soil samples are MnO, Na_2O and P_2O_5.

Table 4.4 also shows that MgO and CaO occur at very low concentrations in the soil samples of all three thermal springs. Because these two oxides are sparingly soluble in water, the high concentrations of Mg and Ca in Mphephu thermal spring and Siloam borehole water samples, shown in Figure 4.2, cannot be entirely accounted for by the concentration of these two elements in the surrounding soil.

Table 4.4 Mass percentage composition of major oxides in Tshipise, Mphephu and Siloam soil samples.

Oxide	Tshipise (%m/m)	Mphephu (%m/m)	Siloam (%m/m)
SiO_2	63.67	85.37	46.28
TiO_2	0.77	0.30	1.58
Al_2O_3	4.26	3.15	12.67
Fe_2O_3	2.77	2.40	12.48
MnO	0.05	0.03	0.17
MgO	2.01	0.31	1.70
CaO	2.75	0.88	2.87
Na_2O	0.24	0.00	0.24

K_2O	1.25	0.32	1.23
P_2O_5	0.29	0.06	0.14

Table 4.4 shows that SiO_2 makes up the bulk of the composition of all three samples, with Mphephu having the largest % composition at 85.37%. This is expected because the soil around the Mphephu thermal spring reservoir was very loose and sandy. According to Table 4.4, soil samples collected from Siloam show a high percentage composition of Fe_2O_3 at 12.48%. Tshipise and Mphephu have an Fe_2O_3 percentage composition of 2.77% and 2.40% respectively. This is expected because the soil at Siloam was deep red in colour, indicative of a high composition of iron in the soil. The other two soil types (Tshipise and Mphephu) were not red in colour, being of a much lighter hew, hence the low percentage compositions of Fe_2O_3 in Tshipise and Mphephu soil samples. Tshipise has the highest percentage composition of P_2O_5 at 0.29% compared to Mphephu and Siloam at 0.06% and 0.14% respectively. This is probably because the site from where the Tshipise soil samples were collected had a lot of vegetation around and was quite dark in colour. The dark colour was indicative of the presence of humus from decomposed vegetation matter. Decomposed vegetation is a potential source of phosphorus in the soil. This phosphorus can then potentially react with dissolved oxygen in soil water forming P_2O_5. Although the Mphephu thermal spring reservoir is surrounded by overhanging branches of trees, the soil is quite light in colour (indicating a lack of humus). In addition, the area immediately around the reservoir generally has sparse vegetation cover. This would explain the low percentage composition of P_2O_5 of 0.06% in the Mphephu soil sample. With titanium being the ninth most abundant element in the Earth's crust and the seventh most abundant metal in the Earth's crust (Kale and Bisaka, 2013), it is therefore unsurprising that all three soil samples have very low mass percentage compositions of TiO_2 as shown in Table 4.4. There are no comparative studies that have been done investigating the oxide composition of soil samples taken from the immediate vicinity of the three thermal springs.

The oxides of toxic elements such as As, Tl, Cd and Pb were not detected. In addition, there were no visible negative effects on the plants growing in the soils surrounding the thermal springs, although these effects are not always visible. Depauperate trees within 2 km of the smelters contained up to 4500 mg L^{-1} Zn and 70 mg L^{-1} Cd in the leaves with no visible effect on the trees (Buchauer, 1973).

4.3.2 Elemental analysis

Table 4.5 shows the concentration (mg kg^{-1}) of select elements obtained from XRF analysis of Tshipise, Mphephu and Siloam soil samples (see other elements in appendix A). Special attention has been given to elements that are toxic at trace concentrations such as Cd and Pb. Sulphur has also been included in the table to emphasise the difference in colour and sample collecting location of the three thermal springs.

Table 4.5 Concentration of select elements found in Tshipise, Mphephu and Siloam soil samples.

Element	Tshipise mg kg^{-1}	Mphephu mg kg^{-1}	Siloam mg kg^{-1}
As	1.90	1.70	2.00
Cd	<DL	<DL	<DL
Tl	0.40	0.00	0.30
Pb	17.80	15.80	18.80
Ce	299.60	11.70	167.50
Cr	65.20	43.70	151.10
V	151.60	64.80	381.60
S	355.90	57.70	114.60

*<DL means less than the detection limit (DL) of the instrument

According to Table 4.5, the Tshipise soil sample has the highest concentration of S at 355.90 mg L^{-1}. Siloam and Mphephu have S concentrations of 114.60 mg L^{-1} and

57.70 mg L^{-1} respectively. This difference is probably because the soil sampling site at Tshipise was surrounded by large amounts of vegetation contributing to its dark (almost black) colour. This dark colour is derived from humus in the soil which in turn is derived from decomposing vegetation. Decomposing vegetation is one of the major sources of S in soil (Assefa et al., 2013). The Mphephu soil sample has the highest levels of SiO_2, making the soil acidic and therefore unsuitable for plant growth. This is probably the reason why there is very little plant growth in the immediate vicinity of the thermal spring. This soil acidity probably contributes to a low S content in the soil due to a lack of decomposing vegetation which in turn is as a result of lack of plant growth in the immediate vicinity of the Mphephu thermal spring. When the CaO content of the Tshipise and Siloam soil samples in Table 4.4 are compared to the S content of the same soil samples in Table 4.5, a direct correlation is shown between an increase in CaO content and a decrease in the S content of the soil. Giel and Bojarczuk (2011) stated that excessive Ca uptake by a plant may lead to various metabolic disturbances within the plant and that it is very important in what form the Ca salts occur in the soil and whether they are soluble in the substrate otherwise very little plant growth (if any) will occur. When compared to the Siloam soil sample, the Tshipise soil sample has a lower CaO content (Table 4.4) and a much higher S content (Table 4.5). However, although Mphephu has the lowest CaO content of the three soil samples, it has the lowest S content of the three soil samples at 57.70 mg L^{-1}. In this case, plant growth in Mphephu soil has been inhibited not by a high CaO content but instead, by the loose sandy nature of the soil, which is unsuitable for plant growth. This is explained by the fact that the Mphephu soil sample has the highest SiO_2 content of all three soil samples (Table 4.4).

Table 4.5 shows that the heavy metals As, Tl and Pb occur at dangerous levels, well above the limits set by various international bodies (Table 2.1). This is alarming because during heavy rains, the soil surrounding the Tshipise and Mphephu thermal spring reservoirs in particular, can be washed into these reservoirs through surface runoff. This can raise the concentration of these heavy metals in the different mineral waters to dangerous levels. Animals and community members that encounter this water could potentially be at risk of heavy metal poisoning.

The element Ce is also of concern due to its cytotoxicity (Wu, 2012). The same author showed that exposure to concentrations of Ce in the range of 23-104 µg g^{-1} not only shortened the lifespan of cells by interfering with various cellular processes but also oxidised these cells and their organelles. Cerium occurs in concentrations well above those investigated by Wu (2012) in all three soil samples. Although the exact mechanism by which Ce is toxic to cells is not yet understood, Wu (2012) further goes on to conclude that Ce toxicity to humans must be taken into consideration nonetheless.

Vanadium is a toxic element that affects organs such as the liver, kidneys, bones and the spleen (Ghosh et al., 2014). The same authors further stated that the side effects of V inhalation are rhinitis, pharyngitis, chronic productive cough, tracheobronchitis and bronchopneumonia. These could be a real possibility when the rains stop and the soils around the thermal springs dry out and are easily whipped about by the wind. In addition, Ghosh et al. (2014) stated that other symptoms of V poisoning include weakness, nose bleeding, vomiting, diarrhoea, dehydration and pulmonary haemorrhage. The MAC for V, according to the Dutch water regulatory authorities, is 5.1 $\mu g\ L^{-1}$ (Smit, 2012). Although the high V concentrations shown in Table 4.5 are in the soil samples, it is conceivable that during the rainy season, much of this soil can be washed into the thermal spring reservoirs through surface runoff. This could raise the concentration of V in the water to dangerous levels.

Durowoju et al. (2016) carried out an elemental analysis of the soil samples taken from the immediate vicinity of Tshipise and Siloam thermal springs. Table 4.6 shows a comparison of the elemental analysis conducted by this study and Durowoju et al. (2016) with regards to the select elements shown in Table 4.5. The concentrations of the elements from the two Siloam soil samples a vastly different. This is probably because Durowoju et al. (2016) sampled at a different Siloam site from the one sampled in this study. According to community members, the main Siloam thermal spring has long since dried up, leaving only separate veins from which to sample from. These veins are now often on the grounds of private households. Therefore, the characteristic elemental signature of the soil sample may well depend from which household the soil samples were collected from. The concentrations of the elements from the Tshipise soil samples, although different, are not vastly different compared to the Siloam soil samples. This is probably because the Tshipise soil samples were collected from different sites that are not too far apart.

Table 4.6 Comparison of two sets of results from soil analysis of Tshipise and Siloam soil samples.

Element	Tshipise		Siloam	
	This work (2018) mg kg^{-1}	Durowoju et al. (2016) mg kg^{-1}	This work (2018) mg kg^{-1}	Durowoju et al. (2016) mg kg^{-1}
As	1.90	0.76	2.00	0.76
Cd	<DL	0.07	<DL	0.17
Tl	0.40	0.04	0.30	0.04
Pb	17.80	13.48	18.80	138.44
Ce	299.60	*	167.50	*
Cr	65.20	54.80	151.10	46.70
V	151.60	115.89	381.60	92.07
S	355.90	*	114.60	*

(*) means elements were absent from the results table

Table 4.7 compares the concentrations of four select elements found in both the soil and water samples from the three thermal springs. A comparison of the concentrations of the elements in both the soil and water samples show there is no correlation between the Tshipise thermal spring, Mphephu thermal spring and Siloam borehole soil and water sample concentrations for all the elements shown in the table. This is probably the case because although the Tshipise and Mphephu thermal spring pools are exposed at the surface to the elements, they are largely closed systems (have been built around) like Siloam borehole and therefore are unlikely to be affected by surface runoff.

Table 4.7 A comparison of concentrations of select elements in soil and water samples.

Element	Tshipise		Mphephu		Siloam	
	Soil	Water	Soil	Water	Soil	Water
As	1.90	13.63	1.70	15.83	2.00	20.97
Cd	<DL	4.63	<DL	8.47	<DL	3.73
Cr	65.20	34.73	43.70	39.90	151.10	62.90
V	151.60	115.47	64.80	213.00	381.60	427.23

*all water concentrations are in µg L^{-1}; all soil sample concentrations are in mg kg^{-1}

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Heavy metals can accumulate in the tissues of the human body over a very long period. This accumulation is toxic and if not treated, will lead to death. The water samples collected from the Tshipise thermal spring, Mphephu thermal spring and Siloam borehole contain three of some of the most toxic elements known to mankind; As, Cd and V. Arsenic occurs at concentrations well above the MAC set by the WHO. As a result, the water from the thermal springs is not suitable for consumption, both in the short and long term. Since the three elements mentioned above cannot be absorbed through the skin, it is therefore safe for tourists to continue bathing in the water. The surrounding soil does not have any impact on the mineral water of these thermal springs.

5.2 Recommendations

Although the water is safe to bath in, some precautions must still be taken such as; Not submerging the head into the water to prevent the water from entering various orifices such as the mouth, the nose, ears and the eyes and avoiding complete contact with the water if there are any open wounds or cuts on the body.

In addition to the precautions that must be taken during bathing in the water, under no circumstances should the water be bottled and sold for consumption. Since the mineral water from Siloam thermal spring is used for activities such as washing dishes, it is recommended that such dishes are thoroughly rinsed in non-Siloam mineral water after washing before use.

Future studies should also include an analysis of elements such as Al, Mn, Ni, Co, Hg and Zn. In addition, future studies should include the effect of seasonal variations on the mineral composition of the water at the thermal springs.

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APPENDIX A

Element	Siloam (mg kg^{-1})	Mphephu (mg kg^{-1})	Tshipise (mg kg^{-1})
Sc	0.3	0.1	0.2
Co	32.1	6.7	7.7
Ni	81.4	32.8	102.3
Cu	164.8	37.9	40.5
Zn	136.8	30.1	71.8
Ga	13.7	4.6	6.6
Ge	1.2	1.2	1.2
Rb	43.3	22.6	29.2
Sr	86.4	32.7	212.3
Y	19.5	9.3	12.0
Zr	144.0	130.9	183.4
Nb	4.4	2.5	6.1
Mo	0.4	0.5	0.4
Ag	0.2	0.5	0.5
Sn	1.7	2.2	2.6
Sb	0.5	<DL	0.2
Cs	9.0	5.4	5.4
Ba	1239.0	284.1	631.1
La	154.3	28.0	35.6
W	<DL	<DL	<DL
Ta	2.1	0.7	0.8
Hf	21.6	10.1	8.4
Bi	0.6	0.4	0.4
Sm	27.9	<DL	<DL
Eu	1.8	0.3	0.5
Gd	42.2	5.5	6.7
Tb	4.7	1.0	1.2
Dy	42.0	8.1	9.3
Er	29.2	5.7	6.5
Yb	47.8	15.5	41.5
Th	6.1	1.0	4.3
U	0.7	<DL	<DL

APPENDIX C

Major oxides	% Composition
SiO_2	48.24
TiO_2	1.39
Al_2O_3	9.54
Fe_2O_3	19.25
MnO	0.3
MgO	0.44
CaO	0.46
Na_2O	0
K_2O	0.33
P_2O_5	0.069

Element	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As
mg kg^{-1}	0	369.1	862.5	49.9	186	259	278	27	1.4	129

Rb	Sr	Y	Zr	Nb	Mo	Ag	Cd	Sn	Sb	Cs
27.8	17.5	10	146.9	2.9	0	1	0	2.1	1.1	5.1

Ba	La	W	Ta	Hf	Tl	Pb	Bi	Ce	Sm	Eu
1106.4	219	20.4	2.8	34	1.4	1196.7	0.9	196	50.3	2.4

Gd	Tb	Dy	Er	Yb	Th	U	S
73.2	8	66	43.9	97	20	2.9	198

APPENDIX B

			Rh (ISTD)	As	Be	Bi	Ca	Cd	Co	Cr	Cu	Ga	Mg	Mn	Ni	Pb	Se	Sr	Th	Ti	U	V	Zn
Type	Sample Name	Dilution Factor	CPS	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]	Conc. [ppb]
QC1	20		106121	20.87	20.52	20.04	20.97	20.83	20.81	19.80	20.07	20.56	20.61	19.89	20.19	20.72	20.52	20.42	20.36	20.23	20.31	20.27	20.97
QC2	100		109465	98.98	97.34	100.1	98.22	97.02	99.85	97.84	98.83	97.98	100.8	98.63	99.95	101.1	97.40	98.18	97.31	98.19	98.75	97.14	102.3
Sample	M1(A)	100	109789				2735						11125										
Sample	M1(B)	100	110454				2768						11158										
Sample	M2	100	111351				2523						10628										
Sample	M3	100	112428				2584						10797										
Sample	S1(A)	100	113469				2511						8657										
Sample	S1(B)	100	113523				2500						8508										
Sample	S2	100	112847				3371						13809										
Sample	S3	100	113654				2733						13872										
Sample	T1(A)	100	115215				850																
Sample	T1(B)	100	114640				824																
Sample	T2	100	114572				827																
Sample	T3	100	116493				799																
Sample	M1(A)	10	103007	1.20	<0.000	<0.000		1.03	<0.000	4.17	4.34	2.75		<0.000	<0.000	<0.000	<0.000	46.3	<0.000	<0.000	<0.000	20.61	<0.000
Sample	M1(B)	10	104818	1.33	<0.000	<0.000		1.23	<0.000	4.52	4.43	2.19		<0.000	<0.000	<0.000	<0.000	46.3	<0.000	<0.000	<0.000	20.25	<0.000
Sample	M2	10	103188	1.54	<0.000	<0.000		1.01	<0.000	3.30	3.50	2.31		<0.000	4.45	<0.000	<0.000	47.2	<0.000	<0.000	<0.000	21.83	<0.000
Sample	M3	10	105371	2.01	<0.000	<0.000		0.50	<0.000	4.50	4.51	2.42		<0.000	5.84	<0.000	<0.000	47.4	<0.000	<0.000	<0.000	21.46	<0.000
Sample	S1(A)	10	106744	2.17	<0.000	<0.000		0.62	<0.000	6.37	2.60	2.59		<0.000	<0.000	<0.000	<0.000	52.0	<0.000	<0.000	<0.000	45.27	<0.000
Sample	S1(B)	10	102597	2.23	<0.000	<0.000		0.59	<0.000	6.04	2.54	2.84		<0.000	<0.000	<0.000	<0.000	50.6	<0.000	<0.000	<0.000	46.57	<0.000
Sample	S2	10	106537	2.24	<0.000	<0.000		0.19	<0.000	5.66	4.49	2.64		<0.000	<0.000	<0.000	<0.000	75.8	<0.000	<0.000	<0.000	38.56	<0.000
Sample	S3	10	105161	1.88	<0.000	<0.000		0.31	<0.000	6.84	7.06	2.38		<0.000	<0.000	<0.000	<0.000	78.6	<0.000	<0.000	<0.000	44.34	<0.000
Sample	T1(A)	10	107823	1.72	<0.000	<0.000		0.64	<0.000	1.50	4.35	3.06	484.92	<0.000	<0.000	<0.000	<0.000	223	<0.000	<0.000	<0.000	11.54	<0.000
Sample	T1(B)	10	107572	1.52	<0.000	<0.000		0.74	<0.000	1.73	4.26	3.18	474.53	<0.000	<0.000	<0.000	<0.000	222	<0.000	<0.000	<0.000	12.47	<0.000
Sample	T2	10	108756	1.52	<0.000	<0.000		0.51	<0.000	3.83	2.81	2.71	471.31	<0.000	<0.000	<0.000	<0.000	220	<0.000	<0.000	<0.000	12.12	<0.000
Sample	T3	10	109327	0.85	<0.000	<0.000		0.24	<0.000	5.09	6.41	2.88	446.06	<0.000	<0.000	<0.000	<0.000	222	<0.000	<0.000	<0.000	10.98	<0.000
QC1	20		109152	20.58	20.10	20.30	19.9	20.12	20.41	19.7	20.44	20.44	20.22	19.59	19.70	19.94	20.66	20.75	19.61	20.46	20.01	19.75	19.72
QC2	100		106351	97.39	96.64	99.34	97.8	96.89	99.79	99.8	98.46	98.70	99.26	96.51	98.55	98.19	97.79	98.92	96.80	98.72	98.94	99.61	101.7