IMPACTS OF TRACE METALS FROM GEOTHERMAL SPRINGS TO THEIR SURROUNDING SOIL AND VEGETATION WITHIN SOUTPANSBERG

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by

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EXECUTIVE SUMMARY

Geothermal springs are natural geological phenomena that occur throughout the world. South Africa is endowed with several springs of this nature. Thirty-one percent of all geothermal springs in the country are found in Limpopo province. The springs are classified according to the residing mountain: Soutpansberg, Waterberg and Drakensberg. This study focused on the geothermal springs within the Soutpansberg region; that is, Mphephu, Siloam, Sagole and Tshipise. The study was aimed at assessing the impacts of trace metals from geothermal springs to their surrounding soil and vegetation in the Soutpansberg region. This study also assessed the potential human health risks associated with trace metals from geothermal springs and surrounding soils in the study areas.

Geothermal springs and boreholes were sampled for a period of twelve months (May 2017-May 2018) to accommodate two major seasons in the study areas. The surrounding soil was sampled vertically from a depth of 10 cm to 50 cm for trace metals concentrations. Three different plants were sampled at each of the study sites, namely, Amarula tree, Guava tree and Mango tree at Siloam; Acacia tree, Fig tree and Amarula tree at Mphephu; Amarula tree, Lowveld mangosteen and Leadwood tree at Sagole; Sausage tree, Amarula tree and Acacia tree at Tshipise. To achieve the objectives, the physicochemical, geochemical and trace metals compositions of the geothermal springs and boreholes (tepid and hot), soils and vegetation were analysed using ion chromatography (IC) (Dionex Model DX 500) and inductively coupled plasma-mass spectrometer (ICP-MS). The temperature, electrical conductivity (EC), pH and total dissolved solid (TDS) of the geothermal springs and boreholes samples were measured *in situ* and in the laboratory. Trace metals analysed in geothermal springs, boreholes, soils and vegetation include Beryllium (Be), Chromium (Cr), Manganese (Mn), Cobalt (Co), Nickel (Ni), Copper (Cu), Arsenic (As), Selenium (Se), Cadmium (Cd), Antimony (Sb), Barium (Ba), Vanadium (V), Zinc (Zn) and Mercury (Hg).

The studied geothermal springs and boreholes are classified according to their temperature as hot and scalding, except for tepid boreholes (treated water). Temperature plays a significant role in the geochemical processes governing groundwater (geothermal springs and boreholes). Piper diagram revealed that most of the geothermal spring water/groundwater (80%) falls in Na-Cl water type except for Siloam geothermal spring with Na-HCO_3 water type, and Tshipise and Siloam community tap water with Ca-Mg-Cl. Durov's diagram corroborates and substantiates more on findings from the Piper's diagram; generally the major water types are Na-Cl and Na-HCO_3 which

are deeper groundwaters (with marine characteristics), influenced by ion-exchange process. Cl^- and Na^+ are the most dominant ions, and the water could result from the reverse ion exchange of Na-Cl waters. Hence making the water type Na-Cl as observed in the Piper diagram. Siloam geothermal spring has $Na\text{-}HCO_3$ water type which is formed as a result of the reverse ion exchange of Na-Cl waters, making Cl dominant anion and Na dominant cation resulting to $Na\text{-}HCO_3$ water type.

The reservoir temperature of all the geothermal springs within Soutpansberg ranged between 95°C to 185°C. Most of the geothermal spring waters are mature except for Siloam geothermal spring water that is peripheral (Durowoju, 2019). Durowoju (2019) reported that the geothermal spring water and boreholes are of meteoric origin (δD and $\delta^{18}O$ values), which implies that rainfall is the fundamental component of these groundwaters. That is, the groundwater was derived from the infiltration of local precipitation, with significant contribution of another type of water in the deeper part of the aquifer (saltwater). The isotopic compositions of groundwater were significantly lighter than those of modern rainwater, indicating that such groundwater could possibly originate from seepage of meteoric water in the past during colder climates.

The geothermal spring waters and boreholes are not fit for drinking due to high fluoride content, except for the treated water such as water from Tshipise and Siloam community tap water. But these waters could be used for direct heating in refrigeration, green-housing, spa, therapeutic uses, sericulture, concrete curing and coal washing. Various indices such as percentage sodium (SP), sodium adsorption ratio (SAR), residual sodium carbonate (RSC), permeability index (PI), Kelly's ratio (KR) and electrical conductivity (EC) were used to evaluate groundwater quality for irrigation. Majority of the indices such as SAR, RSC, PI and EC showed similar results except for KR and SP, implying that the geothermal spring water and boreholes fall under excellent to good category in both seasons. According to Wilcox (US salinity) diagram, all geothermal water and boreholes samples were suitable for irrigation purposes.

The potential health risk associated with trace metals were calculated using USEPA empirical model and does not incorporate clinical study (ecotoxicological study). Hence, further clinical (ecotoxicological) study is necessary to substantiate the findings from the study. The table below summarises the potential non-cancer and cancer health risk calculated from the trace metals concentrations from geothermal springs water and surrounding soils within Soutpansberg.

	Water				Soil			
	Potential Non-cancer Risk		Potential cancer Risk		Potential Non-cancer Risk		Potential cancer Risk	
	Children	Adults	Children	Adults	Children	Adults	Children	Adults
Be	**	**						
V	**							
Cr	**	**	**	**	**		**	**
Mn	**							
Co							**	**
Ni								
Cu								
Zn								
As	**	**	**	**			**	**
Se	**							
Cd			**	**				
Sb								
Ba								
Hg	**	**						
Pb								

** - there is potential of occurrence that need further clinical investigation

From the geothermal springs water, it was found that As, Cr and Cd were the highest contributors to the potential cancer risk with children having a higher risk than adults. Whereas in soils, it was found that Cr, As and Co were the highest contributors to the potential cancer risk in the studied communities. Therefore, the potential cancer risk is high in the general population; that is 1 in 72-162 individuals in children, and 1 in 7-107 individuals for adults. The ingestion route seems to be the major contributor to excess lifetime potential cancer risk followed by the dermal pathway. It is important to emphasise that potential cancer risk indicates the likelihood of trace metals causing cancer but does not confirm cancer unless done through an epidemiological study. Therefore, proper monitoring and control measures to protect human health, particularly in children, should be implemented for safety. The study also explored the use of indigenous trees for phytoremediation and found their uptake capacity to be high, thus, they could be used as bio-indicators to assess the level of contamination of trace metals in the soil. This study has contributed comprehensively towards the advancement and enhancement of the existing knowledge of the geothermal systems, such that water resource management could be applied successfully in the respective areas with similar characteristics for the benefit of the local communities and society at large.

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1. Background

Geothermal springs are natural geological phenomena which occur on all continents. South Africa has about seventy-four known geothermal springs which are associated with rainfall, faulting and shearing (Olivier et al., 2010). Limpopo Province has the highest number of geothermal springs, with about twenty-four known geothermal springs in the country. Durowoju et al. (2015) classified Geothermal springs in Limpopo Province as found in Soutpansberg, Waterberg and Drakensberg Mountains. This study focused on geothermal springs within Soutpansberg, namely Mphephu, Sagole, Siloam and Tshipise.

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

Geothermal springs are usually mineralised depending on the characteristics of the geological formations associated with the circulating groundwater (Todd, 1980). A number of studies have found that geothermal water may contain toxic elements such as arsenic, cadmium, chromium, selenium, and mercury (Manda and Suzuki, 2002; Romero et al., 2003; Churchill and Clinkenbeard, 2005), and radioactive elements such as uranium (U), thorium (Th) and Radon (Rn) (Kempster et al., 1997; Baradács et al., 2001). However, the investigation of the impacts of trace metals from geothermal springs to the surface soil and vegetation is essential since geothermal springs are rich in elements owing to the rock-water interaction in the deep aquifer (Durowoju et al., 2015). The situation is even more worrisome, particularly in South Africa where geothermal springs are under-researched and under-utilised (Olivier et al., 2011). However, geothermal resources are gaining recognition of value even in South Africa as predicted by Olivier et al. (2011).

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

Garzon and Eisenberg (1998); Bonfante et al. (1999); Bortolotti et al. (1999); Capurso et al. (1999); Serio and Fraioli (1999); Fraioli et al. (2001); Bertoni et al. (2002); Grassi et al. (2002); Fioravanti et al. (2003) and Petraccia et al. (2005) have all suggested that geothermal waters are valid tools in the treatment of illnesses such as functional dyspepsia, irritable bowel syndrome and functional disorders of the biliary tract, because carbonated water stimulate the secretion and motility of the digestive tract (Schoppen et al., 2004; Gasbarrini et al., 2006). Furthermore, salt-rich mineral waters enhance the conversion of cholesterol into bile acids and their subsequent secretion (Capurso et al., 1999; Grassi et al., 2002). Spring mineral therapy with sulphurous water can provide beneficial effects in chronic inflammatory disorders with an immunologic pathogenesis by inhibiting the immune response at a local level (Grassi et al., 2002).

Over the past century, there has been an increasing awareness throughout the world of the health and developmental risks associated with environmental exposure to toxic metals, such as, lead (Pb), mercury (Hg), cadmium (Cd), and arsenic (As), due to their toxicity, carcinogenicity, and mutagenicity even at low concentrations (Ifegwu and Anyakora, 2012). While exposure to toxic levels of any of these environmental contaminants may result in impaired health in adults, the toxicological effects of these metals are often more devastating in the development of central nervous system and general physiological systems of children (Countera and Buchanan, 2004).

The use of geothermal spring water for domestic, recreational and agricultural purposes is prevalent in the study communities. Rural communities, such as those at Siloam village produce most of their food on the land on which they live. When agricultural soils are contaminated, these trace metals are taken up by surrounding vegetation and consequently accumulate in their tissues

(Trueby, 2003). To a small extent, trace metals enter the body through food, air, and water and bio-accumulate over a period of time (Hawkes, 1997). Durowoju et al. (2015) showed that geothermal spring can enrich the surface soil with trace metals, which could possibly lead to contamination, particularly where the geothermal spring water is used for irrigation, recreational and agricultural purposes. This makes the community vulnerable to the effects of trace metals emanating from the geothermal spring to human beings via food chain (Aggett, 1998). Hence, there is need to investigate the impacts of the trace metals in the geothermal spring, soil and vegetation.

Therefore, this project is aimed at assessing the impacts of trace metals from geothermal springs to their surrounding soil and vegetation. Also, to explore the target hazard quotients (THQ), Hazard index (HI) and target cancer risk (TR) as deployed by USEPA Region III Risk-Based Concentration Table (US EPA 2004a). The potential health risk associated with these trace metals become highly imperative and were estimated from the measured concentrations of the trace metals from the geothermal springs and surrounding soils using empirical model by USEPA. Hence, this project does not investigate clinical (ecotoxicological) assessment on the inhabitants, which is crucial to substantiate the findings from this study. However, this quantitative study is a conservative assessment tool (pointer) to estimate high-end risk rather than low end-risk in order to protect the public and need further clinical/measurement study to confirm or verify cancer in the population.

1.1 Description of the study areas

Mphephu and Siloam, Sagole, and Tshipise springs are located in Makhado, Mutale and Musina municipalities, respectively, in Vhembe District, Limpopo Province of South Africa (Figure 1.1). The study areas fall under quaternary catchments of the Nzhelele River catchment which is located in the northern region of Limpopo Province, South Africa (Makungo et al., 2010). The study areas are characterised by high-temperature variations in different seasons of the year, with temperatures in winter ranging from 16°C to 22°C, and in summer, from 22°C to 40°C (Makungo, 2008). The mean annual rainfall of Nzhelele ranges from 350-400 mm per annum (Makungo et al., 2010). More than 80% of the rainfall occurs in summer and only about 20% occurs in winter (DWAF, 2001). Brandl (1981) reported that Tshipise and Siloam geothermal springs are underlain by intergranular and fractured aquifer, with borehole yields ranging between 0.1 L/s to 0.5 L/s. Sagole and Mphephu geothermal springs are underlain by fractured aquifers, with borehole yields ranging from 0.5 L/s to 2 L/s (Brandl, 1981).

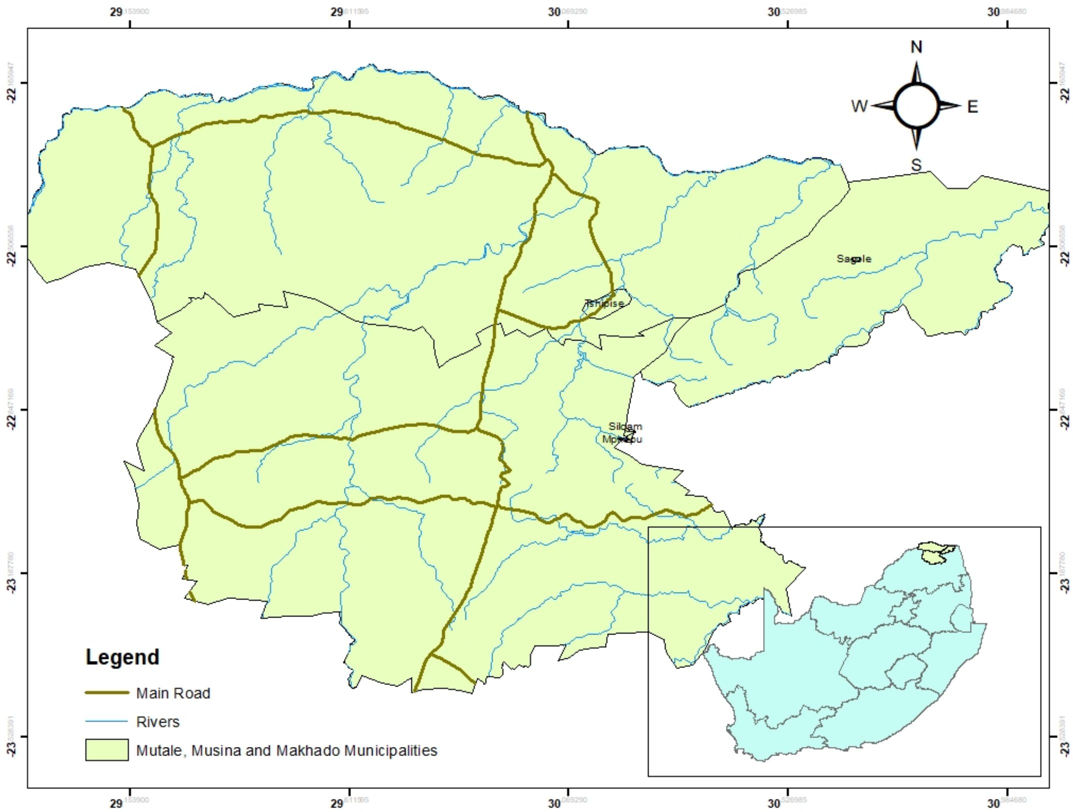


Figure 1: Map of the study areas

1.1.1 Geology of study area

The study area is underlain by block-faulted Karoo Supergroup and Soutpansberg Supergroup rocks in the northern part of the Limpopo Province (Figure 2). These rocks have very low primary porosity, permeability and storage capacity, with limited groundwater flow (Brandl, 1992). Groundwater occurrence is mainly related to secondary hydrogeological features; that is, fault and joints, which present preferential pathways and thus enhance the potential for groundwater flow in the region. The geology determines the extent to which the reaction with the host rock proceeds, depending on the chemical composition of the rock and the rate at which water passes through the rock. Table 1 shows the surface geology and geological structures associated with geothermal springs within the Soutpansberg.

Mphephu geothermal spring is underlain by Wyllie's Poort and Nzhelele Formations of the Soutpansberg Supergroup. These lithologies mainly comprise sandstone and quartzite. Mphephu geothermal spring is associated with the Nzhelele Fault (Brandl, 1981).

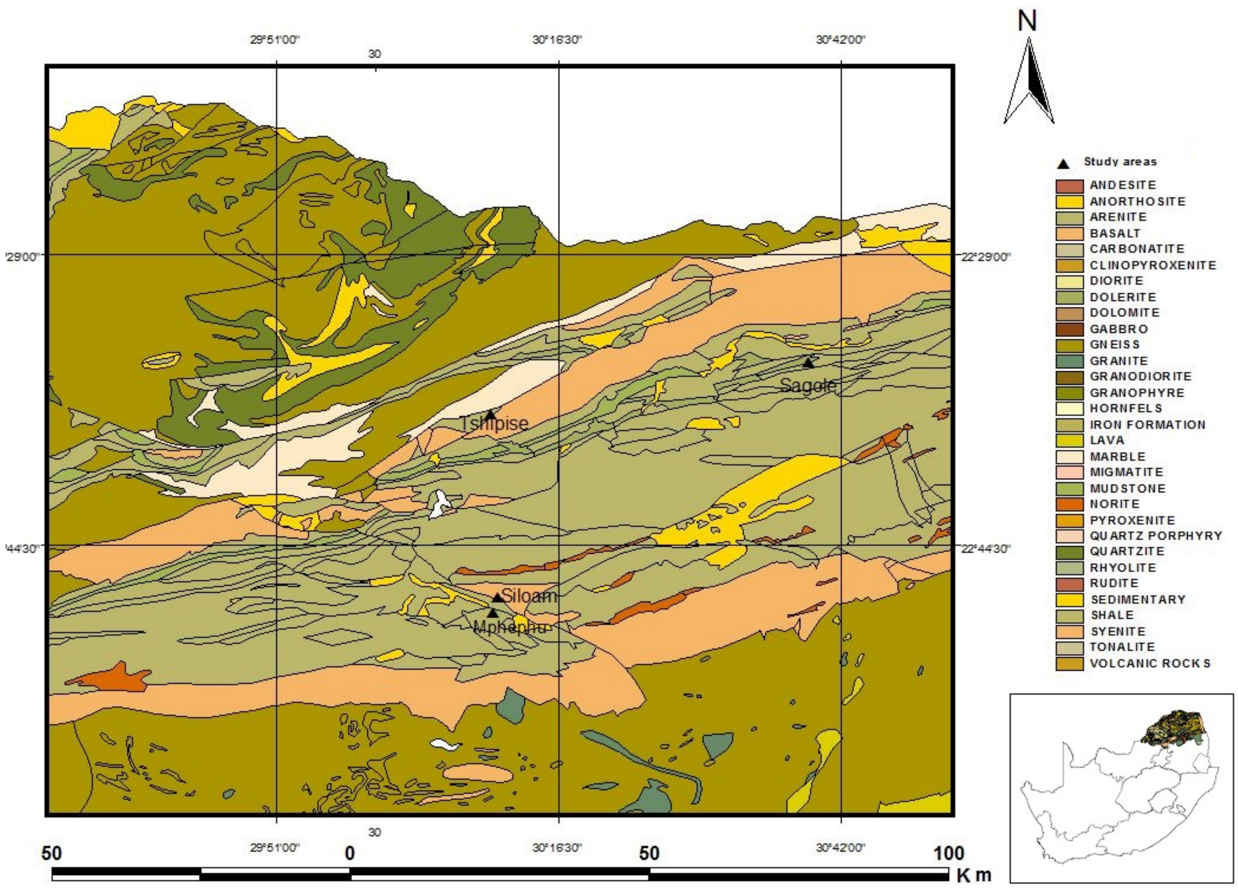


Figure 2: Geology map of study areas

The Sagole geothermal spring is associated with the Klein Tshipise Fault, which lies in the contact zone between Karoo and Soutpansberg Supergroups. To the south of the fault is basalt of the Musekwa Member of the Nzhelele Formation and to the north of the fault are the sedimentary rocks of the Madzaringwe and Mikambeni Formations of the Karoo Supergroup. The Mikambeni Formation consists of mudstone, shale and laminated sandstone, whereas the Madzaringwe Formation comprises alternating sandstone, siltstone and shale, with sporadically occurring coal seams (Johnson et al., 2006).

Table 1: Geology and geological structures associated with geothermal springs

Sampling site	Surface geology and geological structures
Mphephu	Quartzite and Sandstone, Reverse fault between Waterberg Group quartzite and Dominion Reef lava
Sagole	Mudstone, shale, subordinate micaceous sandstone, carbonaceous shale, siltstone, micaceous sandstone. Mikambeni Formation and Madzaringwe Formation, Karoo Supergroup
Siloam	Basalt, minor tuff, Sibasa Formation, Soutpansberg Group
Tshipise	Basalt, minor andesite, cream-coloured sandstone, dolerite sills and dykes Intersection of 2 post-Permian faults in upper Karoo

According to the Geological Survey: 1:250 000 Messina; Kent (1949; 1969)

The Siloam geothermal spring is found in the Nzhelele Valley at Siloam Village, which falls under the youngest Formation of the Soutpansberg Group, which is the Sibasa Formation. It is dominated by basalt, which originated from the lava at the base of the Formation. Basalt is responsible for the more undulating topography to the south of the Soutpansberg (Brandl, 1986). There are dark-red shales and sandstones that are fine, thinly bedded sandstones. There is an interlayer of tuff, ignimbrite and chert and in places tuffaceous shale (Mundalamo, 2003). Various types of conglomerates are also available, such as argillaceous and arenaceous types. The mudstone and siltstone of Delvis Gully Member also exist (Mundalamo, 2003). Siloam Village is characterised by fractured aquifers of sandstone where groundwater occurs.

Tshipise geothermal spring is underlain by basalt and minor andesite of the Letaba Formation of Lebombo Group and Karoo Supergroup. The Lebombo Group rests on the Tshipise member of the Clarence Formation which comprises white to cream-coloured sandstones. These lithologies are intruded by Karoo dolerite dykes and sills, with strongly developed faults (Johnson et al., 2006). The Tshipise thermal spring occurs at the intersection of two post-Permian faults in Upper Karoo, one of which is the Tshipise Fault (Olivier et al., 2011).

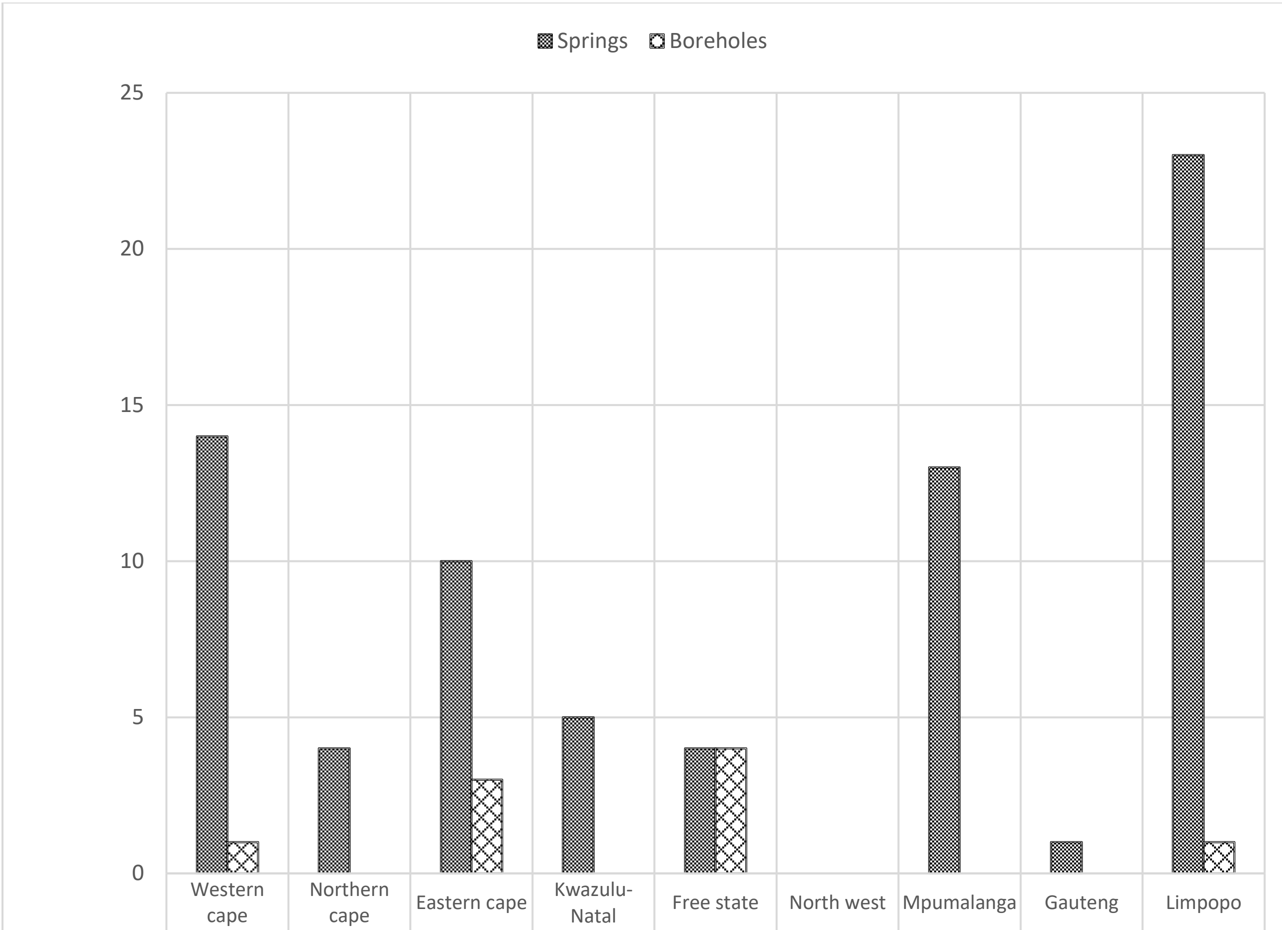
2. Literature review

2.1 Geothermal springs in South Africa

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

Olivier *et al*. (2011) reported the geothermal sources for some of these springs (sulfur springs, Tugela, and Windhoek) or geothermal boreholes and not naturally occurring springs, whereas the geothermal source of other geothermal springs (Vetfontein, Paddysland, Stindal, and Makutsi) could not be located. Figure 3 shows the number of geothermal springs with some associated boreholes per province in South Africa. In South Africa, geothermal spring waters were initially used for domestic and irrigation purposes, and later developed as health resorts and tourism destinations (Hoole, 2001). South African geothermal springs extend into the distant past; for instance, the Khoi (Hottentots) used the geothermal spring at Caledon, calling it 'a fountain of life'. They believed that it could cure any type of illness and if the water was drunk, it made old men become 'active like the younger ones' (Boekstein, 1998). The geothermal spring at Montagu was also frequented by the Khoi and the San (Rindl, 1936).

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



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

Figure 3: *Distribution of geothermal springs and geothermal boreholes per province in South Africa (Olivier et al., 2008).*

2.2 Benefits of geothermal springs

2.2.1 Religious and traditional benefits

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

2.2.2 Medicinal benefits

Medicinal benefits and religious purposes of geothermal springs are interrelated and can be traced back to 2 500 years ago (La Moreaux and Tanner, 2001). Geothermal springs were believed to be a special kind of groundwater owing to its higher mineralisation as well as trace elements, dissolved gases, radioactivity or temperature (Wang and Xie, 2003). Different minerals and gases within the geothermal waters have proven to have different curative abilities. The use of carbolic water is thought to have significant medical importance, for circulatory and heart disorders (Skapare *et al.,* 2003). Sulphated water may heal hepatic insufficiency and problems with the accumulation of organic waste (Skapare *et al.,* 2003). Bicarbonated water may relieve gastrointestinal illness, hepatic insufficiency and gout (Skapare *et al.,* 2003). Sodium chlorinated water may cure a chronic infection of the mucous membrane (Lund, 2000; Skapare *et al.,* 2003).
Ancient Greeks and Roman prescribed drinking and bathing in geothermal springs for its therapeutic effects, especially for ailments such as jaundice and rheumatism (Hoole, 2001; Spicer and Nepgen, 2005). Chinese people used the Huang hot spring on the Shahe River for treatment of various ailments (La Moreaux and Tanner, 2001; Spicer and Nepgen, 2005). The Ethiopians used geothermal springs for the treatment of various diseases, such as skin diseases, leprosy and other contagious diseases (Pankurst, 1990). The ancient Egyptians are believed to have used geothermal baths for therapeutic purposes since 2000 BC. Many of these springs became known as sacred sites, and later evolved as healing centres (Spicer and Nepgen, 2005).

2.2.3 Agricultural benefits

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

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

a) Agricultural crop drying
b) Aquaculture
c) Mushroom farming
d) Heating greenhouses and irrigation

The agricultural uses of the geothermal spring depend on the surface temperature of the spring, which have been summarised in Table 2 below.

Table 2: Temperatures required for various agricultural activities

Temperature in °C	**Agricultural uses**
20-25	Soil heating
35-95	Heating greenhouses
35-95	Food processing
20-40	Aquaculture
35-50	Biogas processing
45-65	Mushroom cultivation
65-95	Drying fruits and vegetables
50-70	Pasteurisation
60-5	Beet sugar extraction
70-100	Blanching and cooking
110-125	Sugar pulp drying

Source: Popovski and Vasilevska, 2003

Geothermal springs can be classified as low temperature (less than 90°C), moderate temperature (90-150°C) and high temperature (greater than 150°C) (Geo-Heat Centre, 2005). South African geothermal springs can thus be classified as low temperature geothermal resources and can be used for activities that require temperatures below 70°C (European Commission (EC), 1999; Geo-Heat Centre, 2005) (as indicated in Table 2). There is real potential for some of these geothermal resources to be used to dry locally produced fruits and vegetables, mushrooms and flowers. Siloam and Tshipise springs are in rural areas and utilising these resources would benefit the rural communities and improve the socioeconomic status of the rural population.

2.2.4 Tourism and recreation benefits

Tourism is one of the catalysts responsible for the development of many geothermal springs into spas or resorts, and many spas are changing their focus to recapture the essence of a true spa's contribution to health and well-being. Currently, about 15 million Europeans immerse themselves daily in geothermal spring waters (Hoole, 2001; Spicer and Nepgen, 2005). Forty-eight countries (e.g. China, Canada, USA, Kenya, Brazil among others) used geothermal springs as resorts in the year 2000 (Lund and Freeston, 2001). These countries do not include those which did not submit data to the Geothermal World Conference of 2000, such as South Africa, Malaysia, Ethiopia, Mozambique and Zambia, though it is known that they do have geothermal springs and spas for recreational use (Lund and Freeston, 2001). Tshibalo (2011) reported that thirty-one (31) out of eighty-three (83) known South African geothermal springs are used for recreation and tourism purposes. Recreational and tourism facilities and activities in South African geothermal spring resorts include the followings: exercise areas, rest areas, restaurants, ladies' bars, shops, solariums, camping facilities, conference facilities, cocktail lounges, picnic sites, golf courses, tennis and squash courts, volleyball, snooker and pool, bowls, heated and cold swimming pools, hot mineral pools, jacuzzis, paddle boats, caravan and camping, game drives, birdwatching, and horse riding (Tshibalo, 2011).

2.3 Health risk assessment of trace metals

Health impact assessment can be defined as the estimation of the effects of a specified action on the health of a defined population (Scott-Samuel, 1998, 2005). According to USEPA (2001, 2004b), human health risk assessment is the process to estimate the nature and probability of adverse health effects in humans who may be exposed to chemicals in contaminated environmental media, now or in the future. The risk assessment process is made up of four basic steps: hazard identification, exposure assessment, toxicity (dose-response) assessment, and risk characterisation (Figure 4).

Hazard Identification involves determining whether exposure to a stressor can cause an increase in the incidence of specific adverse health effects (cancer, birth defects) (Asare-Donkor et al., 2016). It is also used to determine whether the adverse health effect is likely to occur in humans. In the case of chemical stressors such as trace metals (TM), the process examines the available scientific data for a given chemical (or group of chemicals) and develops a weight of evidence to characterise the link between the negative effects and the chemical agent. Exposure to a stressor may generate many different adverse effects in a human such as diseases, formation of tumours, reproductive defects, death, among others (USEPA, 1992, 2002, 2008). One of the major components is evaluating the weight of evidence regarding a chemical potential to cause adverse human health effects.

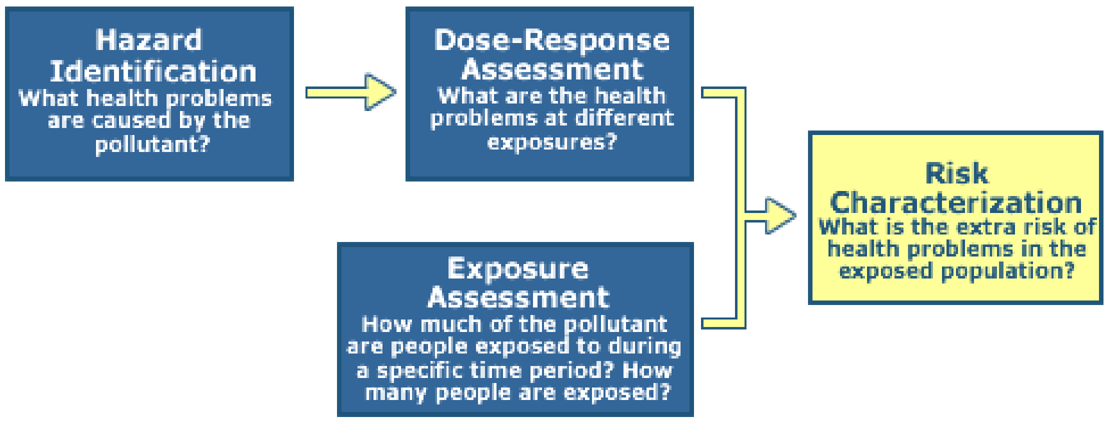


Figure 4: *Four step risk assessment process (USEPA, 2001).*

Dose-Response is the resulting biological response in an organ or organism expressed as a function of a series of doses. It further describes how the likelihood and severity of adverse health effects (the responses) are related to the amount and condition of exposure to an agent (the dose provided). Generally, an increase in dose, increases the measured response. Therefore, at low doses there may be no response and at some level of dose the responses begin to occur in a small fraction of the study population or at a low probability rate. Here are some of the factors that shape the dose-response relationship; agent (e.g. trace metal), the kind of response (e.g. cancer) and the experimental subject (human or animal) (USEPA, 1991, 2001; Asare-Donkor et al., 2016).

Exposure assessment is the process of measuring or estimating the magnitude, frequency, and duration of human exposure to an agent in the environment or estimating future exposures for an agent that has not yet been released (USEPA, 1992). An exposure assessment includes some discussion of the size, nature, and types of human populations exposed to the agent, as well as discussion of the uncertainties in the above information (USEPA, 1992, 2001). Exposure can be measured directly, but more commonly is estimated indirectly through consideration of measured concentrations in the environment, consideration of models of chemical transport and fate in the environment and estimates of human intake over time. Exposure assessment considers both the exposure pathway (ingestion, dermal and inhalation) and the exposure route (means of entry of the agent into the body) (USEPA, 1992; Chrostowki, 1994).

Risk characterisation is the integration of the information on the hazard exposure and dose-response to provide an estimate of the likelihood that any identified adverse effect will occur in the exposed people (Chrostowki, 1994). It conveys the risk assessor's judgment as to the nature and presence or absence of risks, along with information about how the risk was assessed, where assumptions and uncertainties still exist, and where policy choices will need to be made. Risk characterisation takes place in both human health risk assessments and ecological risk assessments (USEPA, 1999).

3. Materials and Methods

3.1 Sample collection, pretreatment and preparation

The project requires field work involving the sampling of the geothermal springs' water, boreholes (tepid and hot), surrounding soils and vegetation (Table 3); sample pretreatment and preparation for chemical analyses. Sampling was carried out for a period of 12 months to accommodate two major seasons in the study areas. It was done once a month (thrice per season), specifically winter (dry) (May-August, 2017) and summer (wet) (October-February, 2018) seasons, to establish the seasonal effect on the parameters (Yahaya et al., 2009). At Siloam, the geothermal spring was sampled for a season because it dried up even till to date. In addition, four boreholes and were samples at Siloam (two of which were hot boreholes and others were tepid boreholes). Also, community tap water was sampled from Siloam and Tshipise, which serves as control. The sampling and pretreatment were carried out using standard procedures and samples were preserved properly for further chemical analyses. Quality assurance/quality control of field samples was carried out for geothermal spring water, soil and vegetation sampling in order to enhance sampling integrity, increase the confidence of analytical data, and prevent reporting positives caused by contamination. Field blank and splits were ensured for water samples, as well as rinsing of blank and splits for soil sample and extract splits for the vegetation samples. Table 3 shows the samples collected from the study sites.

Table 3: Summary of samples and geographic coordinates of the sites

Study sites	Coordinates	Latitude (m)	Type of samples	No of samples per		
				trip	season	Total sample
Siloam	22° 52' 58.80" S	835	Geothermal water	3	06	06
	30° 10' 59.99" E		Surface soil (3 points)	3	06	06
			Sclerocarya birrea (C, B, L)	1	03	03
			Psidium guajava (C, B, L)	1	03	03
			Mangifera indica (C, B, L)	1	03	03
Mphephu	22° 54' 26.28" S	890	Geothermal water	3	06	12
	30° 10' 35.58" E		Surface soil	3	06	12
			Acacia robusta (C, B, L)	3	06	12
			Ficus sycomorus (C, B, L)	3	06	12
			Sclerocarya birrea (C, B, L)	3	06	12
Sagole	22°, 31' 49.44" S	450	Geothermal water	3	06	12
	30°, 39' 07.13" E		Surface soil	3	06	12
			Sclerocarya birrea (C, B, L)	3	06	12
			Garcinia livingstonei (C, B, L)	3	06	12
			Combretum imberbe (C, B, L)	3	06	12
Tshipise	22° 36' 31.32" S	520	Geothermal water	3	06	12
	30° 10' 20.71" E		Surface soil	3	06	12
			Kigelia Africana (C, B, L)	3	06	12
			Sclerocarya birrea (C, B, L)	3	06	12
			Acacia robusta (C, B, L)	3	06	12
Total samples					111	201

3.1.1 Water samples and pretreatment

Geothermal spring water samples were collected from Mphephu, Sagole and Tshipise springs. Siloam spring dried up making sampling exercise not possible but previous data will be used in this study. However, two different boreholes within Siloam Village with similar thermal property as geothermal spring were explored. These boreholes were sampled following standard groundwater sampling procedure (EPA, 2013). Representative samples were obtained through random sampling, in which water was sampled from every part of the spring, where possible with a plastic cup (Figure 5) as recommended by Harvey (2000). The plastic containers were rinsed properly with the spring water to avoid cross-contamination. The samples were kept inside the cooler box and finally stored in the refrigerator at 4°C. All the water samples were collected in 2L plastic containers before transporting them to the laboratory for sample pre-treatment. The water samples were not filtered because there is need to analyse the water in its original status but acidified with concentrated HNO_3 to pH < 2 (normally, 2 mL of concentrated acid per litre) following USEPA (2004). Parameters such as temperature, pH, electrical conductivity (EC), total dissolved solids (TDS) and alkalinity were measured *in situ* and the results are presented in this report. The *in situ* measurement of the geothermal spring water was carried out in triplicate and the average value recorded. The water sample codes are SGW and SGS; TSW and TSS; MPW and MPS in winter and summer for Sagole, Tshipise and Mphephu geothermal springs, respectively. Whereas at Siloam village, there is SAW – geothermal springs, SH1 and SH2 for thermal boreholes, BH1 and BH2 for tepid boreholes and SCC – community treated tap water. Also, TTP represents treated water from municipality at Tshipise.

Figure 5: *Sampling at geothermal spring water*

(i) Sampling water at Mphephu (ii) field instruments and coolers at Sagole (iii) & (iv) measurement of physicochemical parameters at *in situ* conditions (Mphephu, Sagole, Siloam and Tshipise)

3.1.2 Soil Samples and pretreatment

Soil samples for chemical analysis were sampled from the topsoil of depth 0-50 cm with an auger (Figure 6) and were placed in a sampling bag, preferably polypropylene bag as recommended by Pleysier (1995). All soil samples were transported to the laboratory before sample pretreatment. The pre-treatment of soil samples was carried out according to SR ISO 11466:1999. The soil samples were air-dried by breaking down the aggregates, and spreading the soil on a polythene sheet at 25°C. The dried soil samples were ground and sieved through 100 µm sieve. Then, the soil samples were kept in sealed plastic bags to await analysis to be conducted (physicochemical parameters, total trace metal concentration and the water extractable fraction from the saturated paste solution).

The soil sample codes are TSS, SGS, MPS and SMS for Tshipise, Sagole, Mphephu and Siloam, respectively. Although, seasonal variations of the composition were observed; 'W' stands for winter and 'S' stands for summer.

Figure 6: *(i) Sampling soils and (ii) grounding after oven drying at ARC Pretoria*

3.1.3 Vegetation samples and pretreatment

Vegetation samples for chemical analysis were taken from the geothermal spring sites at the study areas. The inner core, root and leaf parts of the plant were sampled owing to their ability to accumulate trace metals from the soil as stated by Pyle et al. (1996) and Robinson et al. (2008). The vegetation samples were handpicked, and a representative sample was achieved by taking a number of sample units randomly and combining them to form a bulk sample (Figure 7). The inner core part of the plant was obtained with a driller. All plant samples were collected and placed in polypropylene bags and transported to the laboratory before the sample pretreatment. The pre-treatment of plant samples (root and leaves) were carried out according to SR ISO 11466:1999. The root and leaf samples were intensely rinsed with tap water and ultrapure water, to eliminate soil and dust from the roots and leaves. Then, the samples were dried at 40°C, ground and then sieved through the 100 µm sieve. The samples were kept in sealed plastic bags awaiting analyses.

Figure 7: *Vegetation samples and pretreatment*

(i)& (ii) sampling the different vegetation, (iii) & (iv) drying the vegetation for grinding at ARC, Pretoria

3.2 Experimental analyses

3.2.1 Saturated soil paste analysis

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

3.2.2 Digestion process

The water samples were not digested because they were acidified during the sample pre-treatment as recommended in USEPA (2004). Samples were further diluted depending on the analyses to be carried out. For ICP-OES analysis (Major cations), there was no further dilution while there was 10 times dilution for ICP-MS analysis (15 trace elements).

The soil samples were digested using a microwave digestion system (SR ISO 11466: 1999) (Figure 6). Approximately 1.0 g of pre-treated samples were digested with 9 mL HNO_3 and 1 mL H_2O_2. The solutions were allowed overnight and placed in the microwave for 30 minutes. After cooling, they were diluted to 50 mL with distilled water.

Figure 8: *Microwave digester and extracts after digestion process at Agricultural Research Council (ARC) laboratory*

The vegetation samples (core, bark and leaves) were digested using Hot Block Method (NIOSH, 2003) (Figure 7). A total of 0.5 g ground samples was weighed and 14 mL of 16 M HNO_3 was added. The solution was allowed to stay overnight and was placed on the block digestion system at initial temperature of 80°C for 30 minutes and increased at intervals of 10°C up to 120°C (Figure 2). Three to four drops of H_2O_2 were added and shaken for a few minutes, then allowed to cool for 20 minutes. Then, it was made up to 100 mL with de-ionised water and filtered with 15 mm size filter paper (ICP-MS analysis).

Figure 9: *Block digestion set up and the extracts at the Agricultural Research Council (ARC) laboratory*

3.2.3 Temperature, pH, EC and TDS analyses

The measurement of the pH, temperature, EC and TDS of the water samples were carried out *in situ* using Multimeter (Multi 340i/SET, USA) and at the laboratory. The temperature of the geothermal spring water was measured *in situ*.

The water extracts obtained from the soil samples were analysed for the pH, EC and TDS following Garltey (2011) procedure. The extracts from soil were further filtered using a 0.45 µm membrane type filter. After calibration of the instrument, the saturated paste extract from the soil samples were analysed for pH, EC and TDS using a Mantech tritrasip autotitrator. All the samples were measured in triplicate and the mean values were estimated per season.

3.2.4 Major anions and cations analyses

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

3.2.5 Trace metals concentration analyses

The geothermal springs and boreholes samples were analysed for trace metals using ICP-MS with a dilution factor of 10. All the measurements were carried out in triplicate to obtain a mean value. The digested samples of the soils and vegetation were ready for analysis. Trace metals were analysed using ICP-MS after the background check up of the equipment (calibration). All the measurements were carried out in triplicate to obtain a mean value.

3.3 Health risk assessment of trace metals

3.3.1 Assessment of health risk from geothermal springs

Common exposure pathways for water are the dermal absorption and ingestion routes (USEPA, 1989; Asare-Donker *et al.,* 2016). Hence, exposure dose to assess the human health risk was calculated using the following equations as adapted from the US EPA risk assessment guidance for Superfund (RAGS) methodology (USEPA, 1989; Asare-Donker *et al.,* 2016).

$$Exp_{ingestion} = \frac{CwaterX\ IR\ X\ EF\ X\ ED}{BW\ X\ AT} \quad \ldots\ldots\ldots\ldots\ldots\ldots 1$$

$$Exp_{dermal} = \frac{(Cwater\ X\ SA\ X\ KP\ X\ ET\ X\ EF\ X\ ED\ X\ CF)}{BW\ X\ AT} \quad \ldots\ldots\ldots\ldots\ldots\ldots 2$$

where, $Exp_{ingestion}$: exposure dose through ingestion of water (mg/kg/day); Exp_{dermal}: exposure dose through dermal absorption (mg/kg/day); C_{water}: average concentration of the estimated trace metals in water (µg/L); Kp: dermal permeability coefficient in water, (cm/h), 0.001 for Cu, Mn, Fe and Cd, while 0.0006 for Zn; 0.002 for Cr and 0.004 for Pb.

Table 4: Exposure parameters used for the health risk assessment through different exposure pathways for water

Parameter	Unit	Child	Adult
Body weight (*BW*)	Kg	15	70
Exposure frequency (*EF*)	days/year	365	365
Exposure duration (*ED*)	Years	6	70
Ingestion rate (*IR*)	L/day	1.8	2.2
Skin surface area (*SA*)	cm^2	6,600	18,000
Dermal Absorption factor (*ABS*)	None	0.001	0.1
Particulate emission factor (*PEF*)	m^3/kg	1.3×10^9	1.3×10^9
Exposure time (ET)	hrs/day	1	0.58
Averaging Time (AT)	Days	365 x 6	365 x 70
Conversation factor (CF)	L/cm^3	0.001	0.001

Source: Asare-Donkor *et al.,* 2016; USEPA, 2009, WHO, 2006

Potential non-carcinogenic risks due to exposure of trace metals were determined by comparing the calculated contaminant exposures from each exposure route (ingestion and dermal) with the reference dose (RfD) (Table 4) using eqn. 3 to generate hazard quotient (HQ) toxicity potential of an individual via the two pathways using eqn. 4 (hazard index).

$$HQ_{\text{ing/dem}} = \frac{Exp_{ing/dem}}{\text{RfD}_{ing/dem}} \quad \text{...3}$$

$$\text{HI} = \sum_{i=1}^{n} HQ_{\text{ing/dem}} \quad \text{...4}$$

Chronic daily intake (CDI) of trace metals through ingestion was calculated using eqn. 5;

$$\text{CDI} = \text{C}_{\text{water}} \text{ x } \frac{IR}{BW} \quad \text{...5}$$

Where C_{water}, IR and BW represent the concentration of the trace metals in water, average daily intake of water and body weight, respectively. Carcinogenic risk (CR) through ingestion pathway was estimated using eqn. 6.

$$CR_{ing} = \frac{Exp_{ing}}{exP_{ing}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 6$$

Where exP is the carcinogenic slope factor and represented in Table 3

3.3.2 Assessment of health risk from surrounding soil

The mean trace metals concentrations were used to estimate intake at the different pathways using standard USEPA's exposure equations (USEPA, 1989; 2004). Children and adult could be exposed to contaminants from soil via three different pathways that include oral intake ($Exp_{ingestion}$), inhalation intake ($Exp_{inhalation}$) and through skin exposure (Exp_{dermal}) (USEPA, 2004). Based on this fact noncancer risk assessment in this study was estimated. For intake estimation via each exposure pathway, the following equations were used;

$$Exp_{ingestion} = \frac{C \ X \ IngR \ X \ EF \ X \ ED}{BW \ X \ AT} \ X \ 10^{-6} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 7$$

where, C – concentration of a contaminant in soil (mg/kg), IngR – ingestion rate of soil (mg/day), EF – exposure frequency (days/year), ED – exposure duration (years), BW – average body weight (kg), AT – average time (days) = ED*365.

$$Exp_{inhalation} = \frac{C \ X \ InhR \ X \ EF \ X \ ED}{PEF \ X \ BW \ X \ AT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 8$$

where, InhR – inhalation rate (m^3/day), PEF – particle emission factor (m^3/kg)

$$Exp_{dermal} = \frac{C \ X \ SA \ X \ SAF \ X \ ABS \ X \ EF \ X \ ED}{BW \ X \ AT} \ X \ 10^{-6} \ldots\ldots\ldots\ldots\ldots\ldots 9$$

where, SA – surface area of the skin that contacts the soil (cm^2), SAF – skin adherence factor for soil (mg/cm^2), ABS – dermal absorption factor (chemical specific) = 0.001(for all metals). After the three exposure pathways were calculated, hazard quotient (HQ) and hazard index (HI) based on cancer/non-cancer toxic risk were calculated as follows (USEPA, 2004):

$$HQ = \frac{Exp}{RfD} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 10$$

$$HI_{ex}P = \sum HQexP \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 11$$

where, exP are Cancer Slope Factors for different exposure pathways, respectively. Reference dose (RfD) (mg/kg/day) is an estimated value of the daily exposure, maximum permissible risk, to the human population, including sensitive subgroups (children) during a lifetime. Tables 5 and 6 show the exposure parameters, reference doses and cancer slope factors used for the health risk assessment for standard residential exposure scenario through different exposure pathways.

Table 5: Exposure parameters used for the health risk assessment through different exposure pathways for soil.

Parameter	Unit	Child	Adult
Body weight (*BW*)	Kg	15	70
Exposure frequency (*EF*)	days/year	350	350
Exposure duration (*ED*)	Years	6	30
Ingestion rate (*IR*)	mg/day	200	100
Inhalation rate (*IRair*)	m^3/day	10	20
Skin surface area (*SA*)	cm^2	2100	5800
Soil adherence factor (S*AF*)	mg/cm^2	0.2	0.07
Dermal Absorption factor (*ABS*)	None	0.001	0.1
Particulate emission factor (*PEF*)	m^3/kg	1.3×10^9	1.3×10^9
Average time (*AT*)			
For carcinogens	Days	365 × 70	365 × 70
For non-carcinogens		365 × ED	365 × ED

Source: Department of Environmental Affairs (DEA), 2010

Table 6: Reference doses (*RfD*) in (mg/kg/day) and Cancer Slope Factors (exP) for the different heavy metals

Heavy Metal	$RfD_{ingestion}$	RfD_{dermal}	$RfD_{Inhalation}$	$exP_{ingestion}$	exP_{dermal}	$exP_{Inhalation}$
As	3.00E-04	3.00E-04	3.00E-04	1.50E+00	1.50E+00	1.50E+00
Ba	2.00E-01	-	2.00E-01	-	-	-
Be	2.00E-04	-	2.00E-04	-	-	-
Cd	1.00E-03	1.00E-03	5.70E-05	6.30E+00	-	6.30E+00
Cr	3.00E−03	3.00E-03	3.00E−05	5.00E−01	-	4.10E+01
Co	2.00E-02	5.70E-06	5.70E-06	-	-	9.80E+00
Cu	3.70E-02	2.40E-02	3.70E-02	-	-	-
Hg	3.00E-04	3.00E-04	8.60E-05	-	-	-
Mn	2.40E-02	1.43E-03	2.40E-02	-	-	-
Ni	2.00E-02	5.60E-03	2.00E-02	-	-	-
Pb	3.50E−03	5.25E-04	3.50E-03	8.50E−03	-	4.20E−02
Sb	4.00E-04	-	4.00E-04	-	-	-
Se	5.00E-03	-	5.00E-03	-	-	-
V	5.04E-03	-	5.04E-03	-	-	-
Zn	3.00E-01	7.50E-02	3.00E-01	-	-	-

Source: DEA, 2010; USEPA, 1989 and 2004

3.4 Data analyses

During the course of this project, many numerical data were generated, which were interpreted so as to achieve the research objectives (Saunders et al., 2012). It is imperative to note that the type of data generated were numerical; therefore, data presentations were done using tables and graphs. The differences and trends; and correlation among the data were carried out statistically using ANOVA, correlation and regression analyses. Multivariate statistics such as principal component analysis (PCA)/factor analysis (FA) and hierarchical agglomerative analysis (HAC) were performed using XLSTAT statistical software (Shan et al., 2012). The PCA was used to establish major variation and relationships among the different trace metals and hydrochemical parameters. Correlation analysis was carried out, and the control was used to ensure the validity of data obtained.

4. Results and Discussion

4.1 Thermal characteristics of the geothermal spring and boreholes

Temperature plays a major role in the chemical composition of geothermal spring waters and the depth at which the water is emanating from (Hartnady and Jones, 2007). The temperature of groundwater provides insight into the subsurface geological processes that generate and transport heat (Witcher, 2002). The classification of springs may also influence usage of the spring, but generally they are classified by surface temperature (Subtavewung *et al*., 2015) as follows; < 20°C (cold spring), 20-29°C (hypothermal/tepid spring), 30-50°C (thermal/hot spring), above 50°C (Scalding/hyperthermia spring). The water temperatures of springs in the study area ranges between 41.3°C and 68.9°C (Figure 10). Based on the above classification; Mphephu and Sagole springs, Siloam (SH1and SH2) boreholes are thermal (hot) water with temperatures ranging between 41°C to 49°C. Siloam and Tshipise geothermal springs can be classified as scalding (hyperthermal) with temperature ranging between 53°C and 69°C. Figure 10 shows clearly the variations in the thermal property of the geothermal springs. Figure 10 indicates that there is no spatial correlation between the location of springs and their geothermal characteristics. Siloam, for instance, has a temperature of 67.7°C, while Mphephu, about 5 km away, has a temperature range of 41-43°C. The same applies to Tshipise and Sagole geothermal springs. This finding supports the literature that geothermal springs in close proximity to each other do not have the same geothermal characteristics (Olivier *et al*., 2010; Durowoju *et al*., 2015).

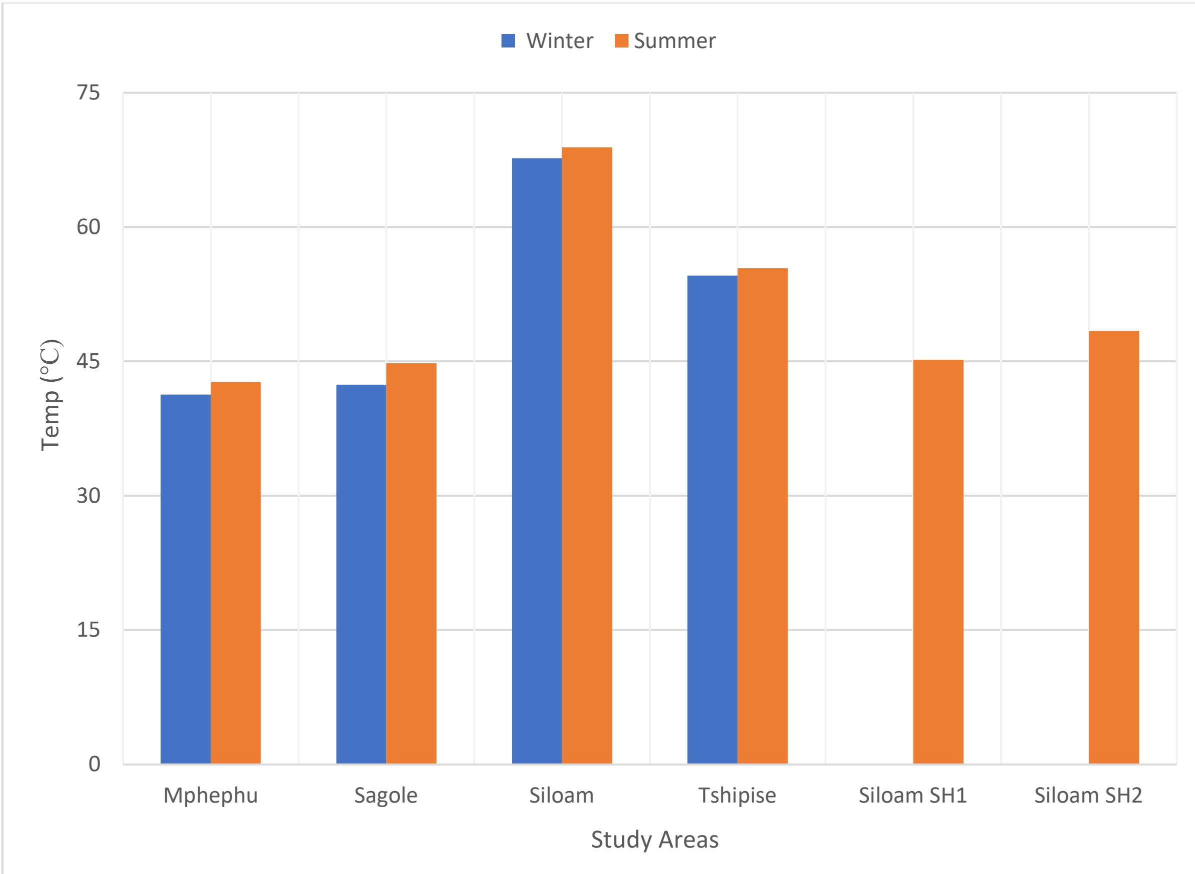


Figure 10: *Mean temperatures of geothermal springs and boreholes within Soutpansberg during winter and summer*

The temperature changes can be attributed to seasonal variation which leads to the fluctuation of the thermal property of the springs. During summer, there is high rainfall and more underground water (coupled with high flow rate), which is heated as a result of the geothermal gradient of 2-3°C per 100 m (Press and Siever, 1986). This implies that geothermal spring water with high temperature emanates from a deeper source. This results in high temperature in summer compared to winter. In all the sites, there is approximately 1°C difference in the thermal property of the geothermal spring in summer compared to winter. These high temperatures in summer result in more transfer of moisture (evaporation and evapotranspiration) to the atmosphere until it reaches the dew point, hence there is potential to rain more intensely during this period. The temperatures of the non-geothermal springs (SCC and TTP) were below 25°C (considered as tepid) and hence, not presented in Figure 10. The geothermal spring waters with lower temperatures are Na-Cl-HCO_3 type waters while the Na-Cl type waters are encountered in high temperature springs (Du *et al*., 2008; Durowoju, 2019). Studies have shown that high water temperature increases vasodilatation in the veins of the skin, thereby accelerating the metabolic processes in the cells of the skin. This, however, improves capillary dilatation and blood circulation, oxygen supply is increased, and the metabolic processes are intensified in the skin and subcutaneous cells (Bjornsson, 2000; Skapare, 2001; Skapare *et al*. 2005). Hence, this is one of the therapeutic purposes of geothermal waters.

4.2 Hydrochemistry of the studied geothermal springs and boreholes

4.2.1 Physicochemical compositions of the groundwaters

Hydrochemical parameters of the geothermal springs, hot and tepid boreholes were used to understand the geochemical processes governing their formation; prediction of sub-surface temperature using chemical geo-thermometers; and to assess suitability of the waters for domestic and irrigation purposes. Table 7 shows the results of the hydrochemical compositions of the geothermal spring water, geothermal boreholes and non-geothermal spring water (tepid boreholes). The hydrochemical compositions of groundwater were not uniform but varied over a wide range. This implies that the groundwater compositions were heterogeneous in nature. This could be attributed to the underlying geology of the study areas (Olivier *et al*., 2011).

TABLE 7: Statistical summary of hydro chemical parameters of geothermal springs/groundwater within Soutpansberg

	SAGOLE		TSHIPISE			MPHEPHU		SILOAM					
	SGW	SGS	TSW	TSS	TTP	MPW	MPS	SAW	SH1	SH2	BH1	BH2	SCC
Temp (°C)	42.4±1.45	44.8±2.12	54.6±2.26	55.4±2.21	22.5±0.00	41.3±1.23	42.7±1.01	67.7±1.68	45.2±0.00	48.4±0.00	22.4±0.00	21.4±0.00	20.1±0.00
pH	8.82±0.95	7.98±0.22	8.46±0.22	8.47±0.21	8.17±0.00	8.05±0.02	8.15±0.07	9.39±0.06	8.86±0.01	9.19±0.00	8.17±0.01	8.10±0.01	7.17±0.02
SAR	33.88±546	19.20±15.48	25.75±0.98	25.45±1.29	0.82±0.01	2.07±0.06	2.18±0.06	7.39±0.04	17.25±0.02	19.04±0.01	4.65±0.01	10.75±0.01	0.28±0.01
EC (µS/cm	330±0.00	347.33±16.17	746.67±5.77	745±7.07	290±0.02	335±7.07	365±21.21	340±2.07	630±0.01	330±0.00	690±0.01	730±0.01	90±0.02
TDS (mg/L)	133.13±1.85	196.70±122.43	377.48±5.36	390.61±7.63	82.99±0.01	124.38±1.41	120.84±1.19	215.18±9.25	305±0.01	130.12±0.1	296.45±0.1	423.07±0.1	10.78±0.10
Alkalinity (mg/L)	10.50±4.24	6.50±5.89	11.12±0.54	10.75±0.35	11.50±0.00	12.50±0.00	6.00±8.49	107.52±1.36	10±0.02	12±0.02	25.50±0.01	17.50±0.01	2±0.02
Na (mg/L)	64.20±1.84	57.13±11.98	157.67±4.51	154.50±4.95	18.30±0.01	42.50±1.27	42.35±1.06	78.77±7.54	118±0.00	62.70±0.01	124±0.03	170±0.01	1.69±0.01
K (mg/L)	1.98±0.01	2.04±0.05	4.55±0.06	4.84±0.05	2.08±0.00	2.06±0.04	2.11±0.01	2.61±0.06	2.73±0.02	2.21±0.1	5.15±0.01	4.67±0.02	1.06±0.01
Ca (mg/L)	0.29±0.11	4.27±6.61	2.84±0.07	2.79±0.10	18.90±0.00	12.20±0.00	11.90±0.28	5.69±0.05	3.53±0.00	0.81±0.01	27.80±0.02	12.80±0.01	0.76±0.01
Mg (mg/L)	0.00±0.00	3.47±6.00	0.00±0.00	0.00±0.00	11.50±0.01	10.50±0.00	10.35±0.07	1.04±0.08	0.00±0.00	0.00±0.00	15.80±0.01	3.72±0.01	1.17±0.2
F (mg/L)	0.77±0.15	2.60±1.71	5.01±0.63	5.98±0.08	0.15±0.01	2.69±0.01	4.16±2.48	6.51±0.08	4.55±0.01	4.95±0.01	4.02±0.01	3.92±0.01	0.00±0.00
NO_3 (mg/L)	0.99±0.36	1.71±0.85	2.13±1.80	5.85±1.48	0.35±0.00	3.02±0.40	6.25±3.23	0.60±0.03	0.17±0.01	1.31±0.01	3.22±0.01	83.95±0.01	0.64±0.01
Cl (mg/L)	41.34±0.30	81.15±75.10	151.86±0.28	156.67±0.02	20.20±0.02	33.90±0.06	98.82±86.34	24.11±0.77	153.3±0.00	38.90±0.01	80.14±0.1	103.23±0.0	3.73±0.01
SO_4 (mg/L)	16.95±0.54	27.89±27.23	45.81±2.15	51.78±0.42	4.11±00	9.21±0.03	21.14±18.31	8.99±0.06	16.45±0.01	10.55±0.01	17.56±0.01	25.88	0.48±0.01
PO_4 (mg/L)	0.92±0.82	13.09±21.49	1.38±1.22	2.14±1.46	0.43±0.00	1.28±0.74	22.6±30.96	0.42±0.06	1.15±0.02	1.52±0.01	3.29±0.02	4.59±0.01	0.17±0.01
CO_3 (mg/L)	1.50±2.12	0.00±0.00	0.58±0.50	0.60±0.42	0.00±0.00	0.00±0.00	0.00±0.00	16.13±0.41	1.80±0.01	2.40±0.01	0.00±0.00	2.70±0.00	0.00±0.00
HCO_3 (mg/L)	9.76±0.86	7.93±7.19	12.38±0.37	11.90±0.43	14.03±0.01	15.25±0.00	7.32±10.35	98.75±2.08	8.54±0.02	9.76±0.02	31.11±0.00	15.86±0.00	2.44±0.00

SGW-Sagole (Winter), SGW-Sagole (Summer), TSW-Tshipise (Winter), TSS-Tshipise (Summer), MPW-Mphephu (Winter), MPS-Mphephu (Summer), SAW-Siloam (geothermal spring), SH1- Siloam (Hot borehole), SH2- Siloam (Hot borehole), BH1- Siloam (tepid borehole), BH2-Siloam (tepid borehole), SCC-Siloam (Community borehole), TTP – Tshipise (treated tap water)

Results showed that geothermal springs, hot and tepid boreholes were more mineralised than SCC and TTP. This could be attributed to the rock-water interaction at the deeper aquifer leading to more mineralisation of the geothermal springs (Todd, 1980, Durowoju *et al*., 2016b). Interestingly, Siloam hot and tepid boreholes show a similar variation in hydro-chemical parameters with geothermal spring and this could be attributed to underlying geology or aquifer connectivity. Non-geothermal water (SCC and TTP) falls within domestic water quality (DWAF, 1996) and WHO (2000) value for pH, sodium adsorption ratio (SAR), electrical conductivity (EC) and total dissolved solids (TDS).

Generally, the measured pH values range from 7.17 to 9.39 which implies that the waters are alkaline in nature. Most of the groundwater pH falls within recommended South African National Guidelines for Domestic Water Quality (DWAF, 1996; SANS, 2015) values of 7-9 except for Siloam geothermal spring water (SAW) and Siloam hot borehole (SH2) having pHs of 9.39 and 9.19, respectively. The TDS values were generally less than 450 mg/l ranging from 10.8 to 423 mg/l for all the samples with a slight difference across seasons. Hence, the TDS values fall within the South African Guidelines for Domestic Water Quality (DWAF, 1996) value of 450 mg/L. Although, previous studies showed that the TDS values for Tshipise geothermal spring was found in higher than 450 mg/L (Olivier *et al*., 2011; Durowoju *et al*., 2018), this study recorded a lower value than then. This could be as a result of the decrease in water temperature of the spring in the present study (decreased from 58°C to 55.7°C).

The dominant ionic compositions found in the site waters are sodium (Na^+), bicarbonate (HCO_3^-), sulphate (SO_4^{2-}) and chloride (Cl^-) (Table 6). The concentrations of sodium (Na^+), chloride (Cl^-) and sulphate (SO_4^{2-}) were highest in Tshipise (TSW and TSS). At Siloam village, BH1 and BH2 (tepid water) were found to have higher Na^+ concentrations than SAW (geothermal spring); though, Na^+ concentrations in Siloam were generally high except for the community borehole (SCC) that is already treated from the municipality. The high Na^+ concentrations probably originate from the dissolution of sodium-rich plagioclase feldspars (albite) in the sandstone and shale. The general order of dominant cations is $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$ and the sequence of the abundance of the anions are in this order: $Cl^- > SO_4^{2-} > HCO_3^- > F^- > NO_3^- > PO_4^{3-}$. These uneven distribution of the hydro-chemical parameters play a vital role in understanding the processes governing the system as well as the suitable benefits of these springs, considering the fact that these geothermal springs are in the rural communities, where the community members see the springs as a viable source of water and they use it for various purposes including drinking, domestic, and irrigation among others.

4.2.2 Water types

In order to understand the geochemical evolution of groundwater in the study areas, the samples were plotted on a Piper's diagram (Piper, 1944) and Durov's diagram (Durov, 1948) using Geochemist's Workbench version 11.0.7 (GWB 11) software. Piper diagram is a multifaceted plot wherein milliequivalents percentage concentrations of major cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) and anions (HCO_3^-, SO_4^{2-}, and Cl^-) are plotted in two triangular fields, which were then projected further into the central diamond field (Ravikumar *et al.,* 2015). In contrast, Durov diagram is a composite plot consisting of two ternary diagrams where the milliequivalents percentages of the cations of interest were plotted against those of anions of interest; sides form a central rectangular, binary plot of the total cation against total anion concentrations (Ravikumar *et al.,* 2015). Both diagrams were used in this study to understand hydro-chemical processes involved along with the water type of the geothermal spring/groundwater. Durov's plot was used to validate the water types and the process of formation. The Piper's diagram revealed that most of the geothermal spring water/groundwater (80%) falls in Na-Cl water type except for Siloam geothermal spring (SAW – WT29 and WT30) which is a Na-HCO3 water type, and for TTP (Tshipise tap water) and SCC (Siloam community borehole) is Ca-Mg-Cl (Figure 11). Interestingly, this study findings are in line with the recent findings by Durowoju *et al*. (2018) but differs from Olivier *et al*. (2011) which reports $NaHCO_3$ and Na-Ca-HCO_3 water types for Sagole and Mphephu springs, respectively. This could be as a result of convergence outcomes obtained from both Piper plot and Durov plot, which corroborate each other and validate the findings. Also, small sample size collected (sampled in 2004 and 2010) by Olivier et al. (2011) as well as source rock interaction could be responsible for the difference obtained.

Na-Cl water type is dominated by Na^+ and Cl^-, derived from Na-Cl brines in winter and summer linked to the underlying geology emanating from gneissic rocks. Na-Cl and Na-HCO_3 water types showed a typical marine and deeper ancient groundwater influenced by ion exchange. The Na-HCO_3 water type from Siloam geothermal spring showed that the spring emanates from basaltic rocks. It is the most evolved of the waters and it derives its Na^+ from cation exchange of Ca^{2+} for

Na^+ and K^+ as well as dissolution of rock minerals (plagioclase) (Lipfert *et al.,* 2004). TTP and SCC with Ca-Mg-Cl water type demonstrate the dominance of alkaline earths over alkali (Ca+Mg > Na+K) and strong acidic anions over weak acidic anions ($Cl+SO_4 > HCO_3$).

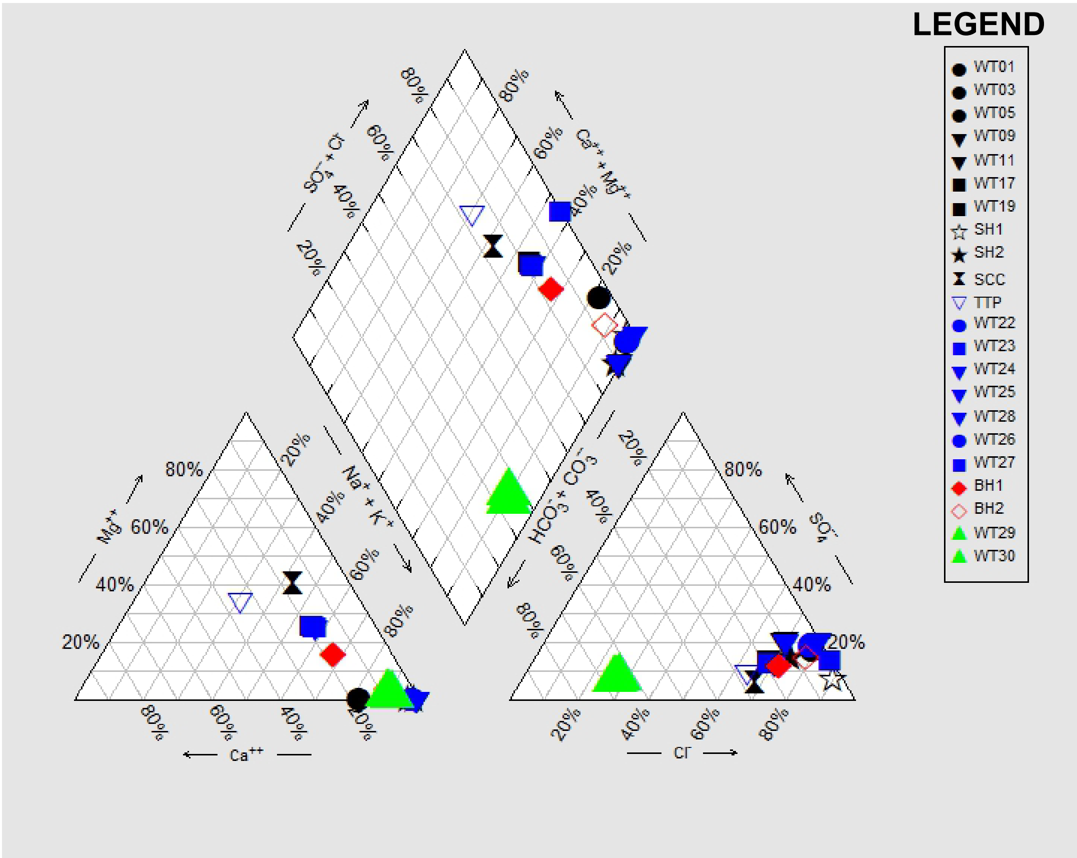


Figure 11: *Piper diagram of geothermal springs and boreholes within the Soutpansberg region.*

Durov's diagram corroborates the findings from the Piper's diagram (Figure 12). Most of the geothermal spring/groundwater has Cl^- and Na^+ dominating and the water could result from the reverse ion exchange of Na-Cl waters. Hence making the water type Na-Cl as observed in the Piper diagram. As observed from Piper's diagram, Siloam geothermal spring (SAW) has Na-HCO_3 water type which is formed as a result of the reverse ion exchange of Na-Cl waters, making Cl^- a dominant anion and Na^+ a dominant cation making the water Na-HCO_3 (Durov's diagram). Na-HCO_3 could be formed as result of ion exchange process of $CaCO_3$ (carbonated rock) within the aquifer. The TTP and SCC have no dominant anion and cation which indicates that the water exhibits simple dissolution or mixing compared to the geothermal spring water and other boreholes. Durov's diagram further explains the geochemical processes leading to the respective water type, hence, the advantage of the Durov's diagram over the Piper's diagram. The major water types are Na-Cl and Na-HCO_3 which are typical of marine and deep groundwaters which are influenced by the ion-exchange process.

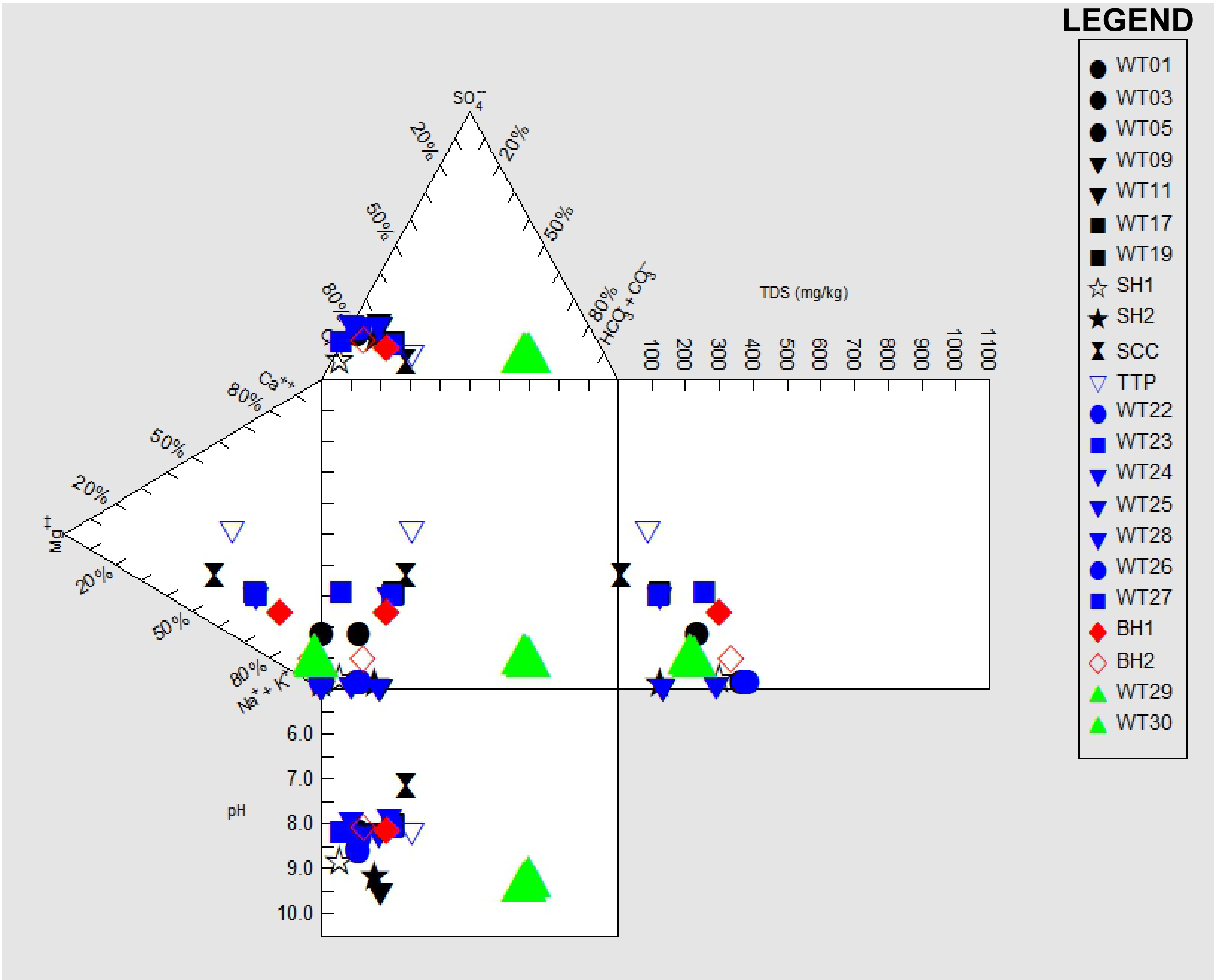


Figure 12: *Durov diagram of geothermal springs and boreholes within Soutpansberg region.*

There is no variation in the water type with season for the studied geothermal spring/groundwater. The Na^{+} and HCO_3^{-} ions were also present, making the water type fall under class C (temporary hard carbonate water) (Bond, 1946) as reported by Olivier *et al*. (2011). Hence, the presence of Na+ in groundwater in the area due to water-rock interaction as a result of oxidisation and evapotranspiration processes. These findings support the previous studies by Durowoju *et al*. (2018).

4.2.3 Geochemical processes controlling groundwater chemistry

The geochemical processes controlling the geothermal spring chemistry were demonstrated by Gibbs (1970). Gibbs plot provides vital information on the mechanisms (precipitation, rock-water interaction or evaporation) controlling groundwater system by plotting the EC against Na/Na+Ca and $Cl/Cl+HCO_3$. Figure 13 shows that all the geothermal springs/boreholes plotted in rock-water interaction zone, as reported by Durowoju *et al*. (2018) for Siloam and Tshipise springs. Thus, the groundwater chemistry in the studied areas is controlled mainly by rock-water interaction processes caused by the chemical weathering of the rock-forming minerals. Hence, this implies that weathering of aquifer material is the dominant process controlling the chemistry of the springs resulting in chemical budget of this water (Aghazadeh and Modaddam, 2010). Along the path of groundwater movement from recharge to discharge areas, several chemical reactions take place with the solid phase. These chemical reactions vary temporally and spatially, depending on the chemical nature of the initial water, geological formations and residence time (Aghazadeh and Modaddam, 2010).

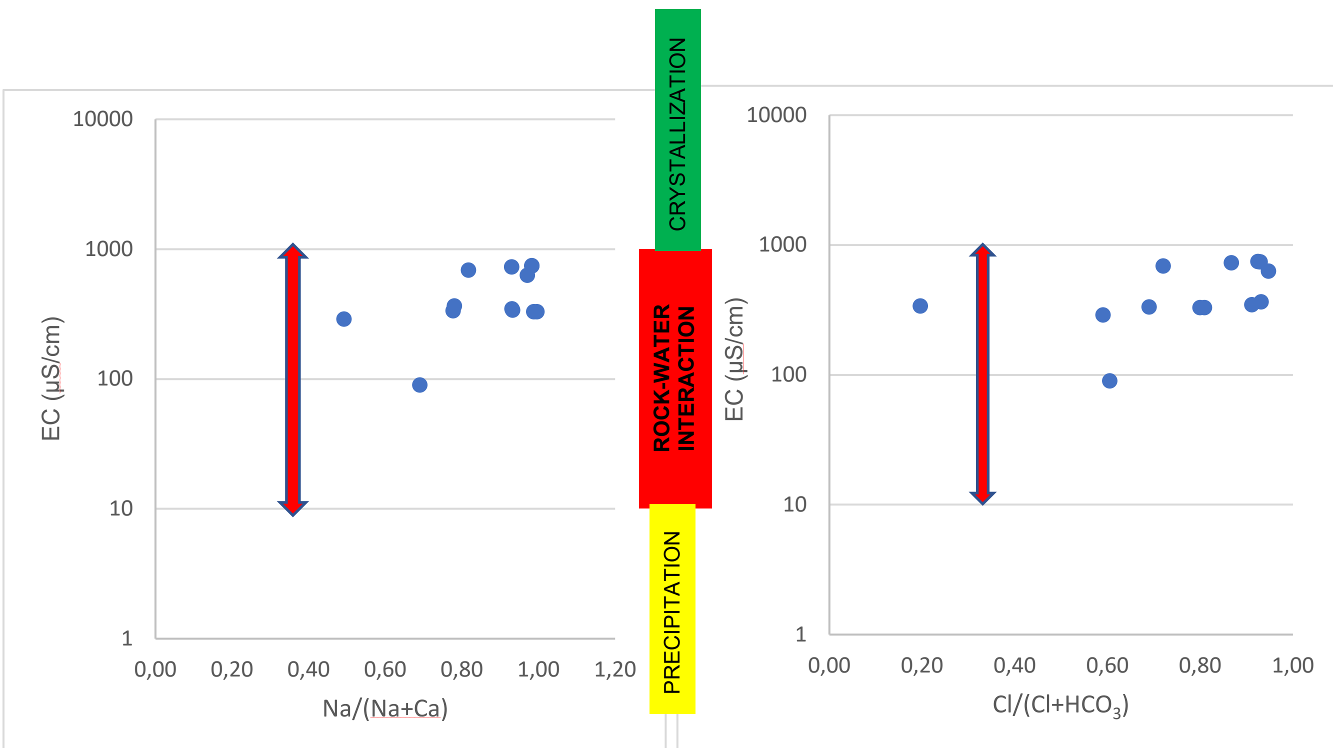


Figure 13: *Mechanisms controlling chemistry of the geothermal springs and boreholes-Gibbs plot of samples in blue shaded circles*

Datta and Tyagi (1996) and Lakshmanan *et al*. (2003) revealed that the plot of (Ca + Mg) against (HCO_3+SO_4) is also another tool to determine geochemical processes. It shows the distribution of geothermal water/borehole water between silicate and carbonate weathering processes that are used to assess the effects of the carbonate and sulfate mineral dissolution in the system (Figure

12), by distinguishing between carbonate and silicate weathering controlling factors. The water samples are distributed below and above the 1:1 line, which shows they are in the field of silicate or carbonate weathering (Figure 14). This contradicts findings from Durowoju *et al*. (2018), which reported that Siloam and Tshipise geothermal springs fall in silicate weathering zone. This could possibly be as a result of the sample size and instability of the rock-water interaction leading to these chemical weathering. Those groundwater samples that fall above the 1:1 line resulted from the effect of reverse ion exchange in the system which indicate carbonate weathering processes supporting the Gibb's diagram.

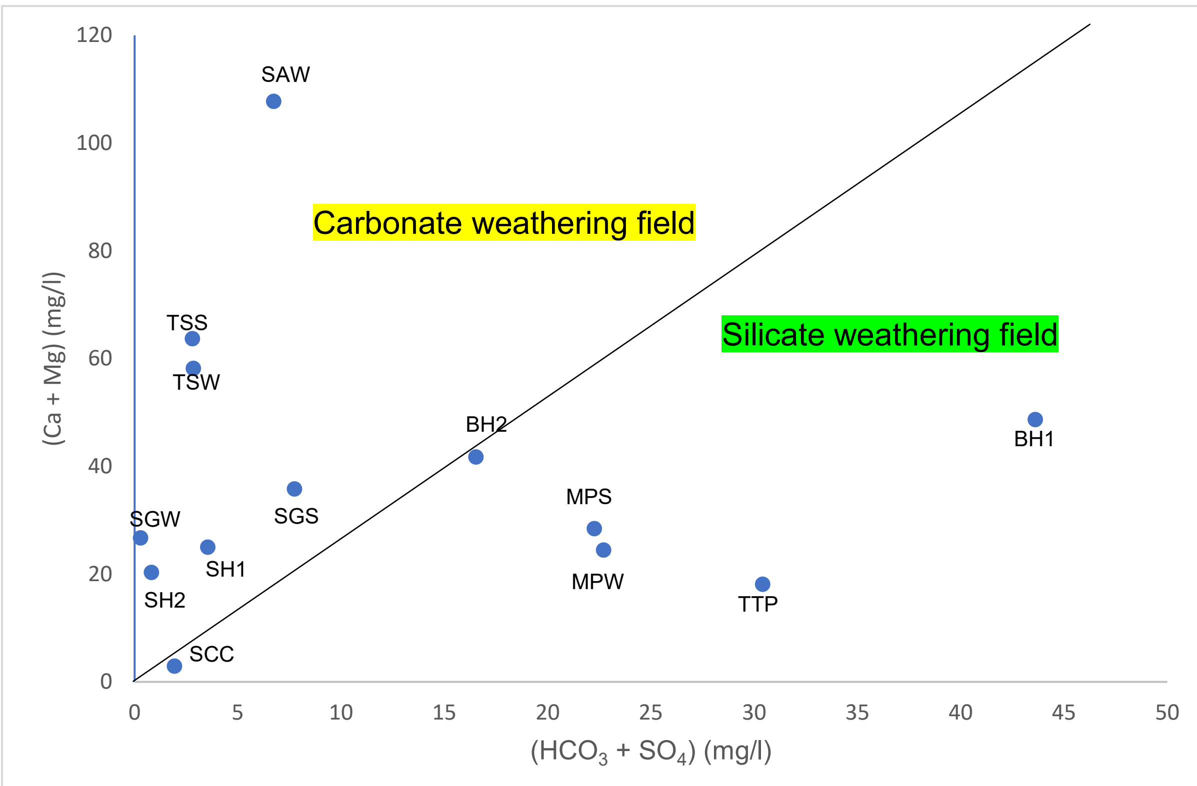


Figure 14: *Plot of (Ca+Mg) vs (HCO_3+SO_4) for the geothermal springs/boreholes' samples within the Soutpansberg region.* ● *Samples of geothermal spring and /boreholes*

Samples that fall above the 1:1 line mostly include geothermal springs, except for Mphephu (MPW and MPS) (Figure 14). All the tepid water (BH1, BH2, SCC and TTP) and Mphephu geothermal water fall below 1:1 line which indicates silicate weathering. This further shows the contributions of the cation exchange, and carbonate and sulfate minerals dissolutions. There is the possibility that hot boreholes (SH1 and SH2) at Siloam share the same geochemical processes with the geothermal spring (SAW) suggesting interconnectivity between the two aquifers. Therefore, ion exchange processes between groundwater and the aquifer materials are relatively high. Hence, this shows that the plot of (Ca + Mg) against (HCO_3+SO_4) is in good agreement with Gibb's diagram. The chloro-alkaline indices (CAI 1, 2) indicate the possible ion exchange reaction between the groundwater and their host environment as suggested by Schoeller, (1977). Chloro-alkaline indices used in the evaluation of base-exchange are calculated using equations 12 and 13.

$$CAI\text{-}1 = Cl - (Na + K)/Cl \quad \text{...12}$$

$$CAI\text{-}2 = Cl - (Na + K) / (SO_4 + HCO_3 + NO_3) \quad \text{... 13}$$

Among CAIs, CAI-1 varied from -2.36 to 0.55 and CAI-2 ranged from -1.08 to 1.57, which were negative in most samples (80%) suggesting the presence of base-exchange processes. Ca^{2+} and Mg^{2+} exchange with Na^+ sorbed on the exchangeable sites on the aquifer minerals, resulting in the decrease of Ca^{2+} and Mg^{2+} and increase of Na^+ in the groundwater by reverse ion exchange (Schoeller, 1977; Glover *et al.,* 2012). This confirms that Ca^{2+}, Mg^{2+} and Na^+ concentrations are interrelated through reverse ion exchange. Similar results were obtained in Northwestern China, which indicates cation-anion exchange (chloro-alkaline disequilibrium) (Liu et al., 2015). The results indeed clearly show that Na^+ and K^+ are released by the Ca^{2+} and Mg^{2+} exchange, which are common forms of cation exchange in the study areas. The remaining 20% of samples, which had positive CAIs, indicated direct exchange of Ca^{2+} and Mg^{2+} from the aquifer matrix with Na^+ and K^+ from the groundwater. This shows that the cation exchange is one of the major contributors to higher concentrations of Na^+ in the groundwater.

Table 8 presents the correlation between the physicochemical and geochemical data in the studied areas. This is achieved by calculating the Pearson correlation coefficients with unevenly distributed data (Locsey and Cox, 2003). A strong relationship exists between pH, alkalinity, F^-, CO_3^{2-} and HCO_3^-; which implies that the waters are more alkaline. High F^- concentrations are associated with alkaline medium, hence, this explains the presence of high F^- content in the studied groundwater. There are strong positive correlations between total dissolved solids (TDS) and cations such as Na^+ and K^+; anions such as F^-, Cl^-, NO_3^- and SO_4^{2-}. Temperature shows a weak correlation with Na^+, K^+, Cl^-, SO_4^{2-} and HCO_3^-; and a strong correlation with F^- and CO_3^{2-}. This implies that temperature favours the dissolution of soluble solid in the water.

Table 8: Pearson correlation matrix of correlation among physiochemical variables in geothermal water and boreholes

	Temp	pH	SAR	EC	TDS	Alkalinity	Na	K	Ca	Mg	F	NO_3	Cl	SO_4	PO_4	CO_3	HCO_3
Temp	1.00																
pH	**0.71**	1.00															
SAR	0.49	0.47	1.00														
EC	0.13	0.21	0.38	1.00													
TDS	0.22	0.25	0.42	**0.96**	1.00												
Alkalinity	0.48	**0.55**	-0.15	-0.04	0.10	1.00											
Na	0.22	0.29	0.47	**0.96**	**0.99**	0.09	1.00										
K	0.03	0.13	0.25	**0.94**	**0.90**	0.08	**0.91**	1.00									
Ca	***-0.54***	-0.25	***-0.60***	0.22	0.08	0.06	0.05	0.36	1.00								
Mg	***-0.52***	-0.37	***-0.68***	-0.04	-0.20	-0.08	-0.23	0.09	**0.93**	1.00							
F	**0.69**	**0.61**	0.23	**0.61**	**0.66**	0.48	**0.66**	**0.57**	-0.09	-0.24	1.00						
NO_3	-0.37	-0.16	-0.06	0.40	**0.50**	-0.03	0.49	0.42	0.19	-0.01	0.09	1.00					
Cl	0.29	0.13	0.47	**0.85**	**0.82**	-0.25	**0.79**	**0.67**	-0.09	-0.22	**0.57**	0.19	1.00				
SO_4	0.40	0.09	**0.62**	**0.76**	**0.77**	-0.19	**0.75**	**0.70**	-0.19	-0.29	**0.52**	0.17	**0.84**	1.00			
PO_4	0.02	-0.23	-0.17	-0.06	-0.09	-0.22	-0.14	-0.12	0.14	0.30	0.08	0.07	0.21	0.18	1.00		
CO_3	**0.55**	**0.62**	-0.05	-0.09	0.08	**0.96**	0.07	-0.03	-0.16	-0.30	0.48	0.02	-0.24	-0.20	-0.22	1.00	
HCO_3	0.45	**0.52**	-0.19	-0.02	0.11	**1.00**	0.09	0.12	0.14	0.00	0.47	-0.05	-0.25	-0.18	-0.21	**0.93**	1.00

Values in bold are different from 0 with a significance level alpha=0.05

Fluoride shows a very strong positive correlation with Na^+ and K^+ but weak negative correlation with Ca^{2+} and Mg^{2+}. This also justifies the presence of high F^- content in the groundwater/geothermal spring water since the most dominant cation is sodium (Durowoju *et al*., 2015). There is also a strong correlation between Na^+ and other anions such as F^-, Cl^- and $SO4^{2-}$. This further justifies the fact that Na-Cl water type is mostly the dominant water type in the studied geothermal water/groundwater. As explained earlier, this water type is characteristic of deep groundwater that is influenced by ion exchange processes (Durowoju, 2019).

The plot of Na^+ against Cl^- is used to establish the role of evaporation for higher concentration of Na in the groundwater (Figure 15). Gurdak *et al*. (2007) reported that the influence of semi-arid climate as intercalation in the soil zone enhances active evaporation in the study area. This implies that, there is loss of groundwater quantity during summer by the action of evaporation resulting in an increase in salt concentration in the groundwater.

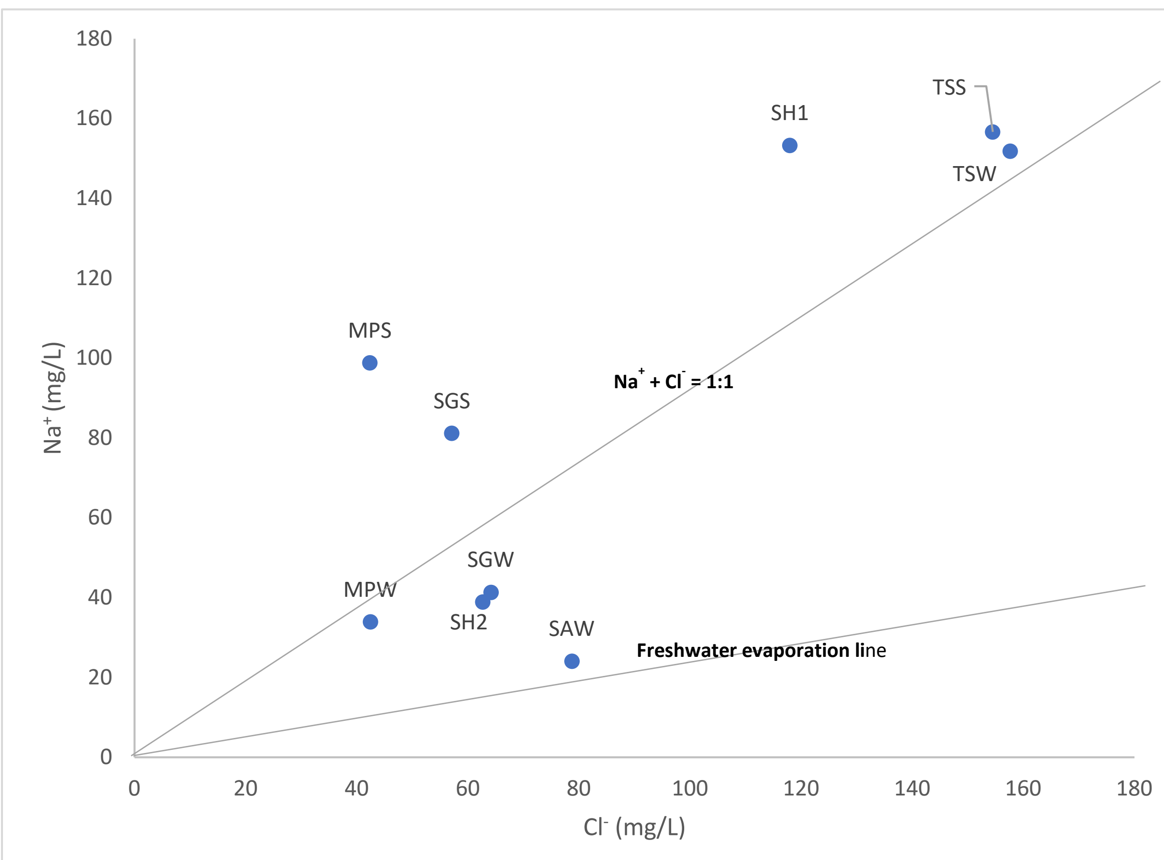


Figure 15: *Relation between* Na^+ *and* Cl^- *in the geothermal springs within the Soutpansberg region*

All groundwater samples plotted above the freshwater evaporation line including data sourced from literature around the world (Figure 15). This indicates that evaporation is one of the processes, controlling the geochemistry of geothermal spring (Gurdak *et al*., 2007).

4.3 Evaluation of geothermal springs and boreholes quality for drinking, domestic and irrigation purposes

4.3.1 Suitability for drinking and domestic purposes

Geothermal spring water is found in rural communities, where it serves as an alternate source of domestic water. The community uses spring water for drinking and domestic purposes without proper understanding of its composition and potential health effects. Hence, there is need for sustainability and maintenance of the quality of geothermal spring water for drinking as it is one of the targets of the Sustainable Development Goals (SGDs), 2016. Therefore, the water quality is assessed in comparison with national and international accepted permissible drinking water quality limits (WHO, 2006).

Results were obtained to ascertain the suitability of the geothermal water/groundwater in the studied areas for drinking and domestic purposes based on the South African Bureau of Standards (SABS, 1999) and World Health Organisation (WHO, 2004; 2006) standards (Table 9). Although, pH values have no effect on human health, it remains a crucial parameter because it affects other chemical constituents of water. Most of the geothermal water/groundwater falls within the recommended permissible drinking water limit with regard to pH except for Siloam geothermal spring (SAW) and Siloam hot borehole (SH2) water. The following hydrochemical parameters in all geothermal water/groundwater fall within guidelines recommended by the WHO and SANS for drinking water; EC, TDS, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-} and HCO_3^{-}. Whereas, fluoride concentrations were higher than the recommended guidelines except in Sagole geothermal spring (SGW – 0.77 mg/l), Siloam community water (SCC – 0.00 mg/l) and Tshipise tap water (TTP – 0.15 mg/l). SCC and TTP are both treated water, hence they contain little or no fluoride. Also, the NO_3^{-} concentration in all the samples were within the permissible limit for drinking water except for Siloam borehole (BH 2). This could be attributed to anthropogenic factors (proximity to the pit latrine, application of fertilizer among others) within the vicinity of the borehole (Odiyo and Makungo, 2018). Generally, the geothermal water/ groundwater is not fit for drinking due to high fluoride content (Odiyo and Makungo, 2012), except for the treated water such as water from SCC and TTP. This study also confirms previous findings from Olivier *et al*. (2011) and Durowoju (2015) that the geothermal spring water are not fit for drinking purposes unless their quality is evaluated and where necessary treated to compliance. Generally, the utilisation of the geothermal springs across the world is solely dependent on the chemical compositions. Hence, this study recommends that the geothermal springs within the Soutpansberg region should be used for direct heating in refrigeration, green-housing, spa, therapeutic uses, sericulture, concrete curing and coal washing. They could also be used for drinking and cooking if the fluorides and nitrates are managed where there are high non-compliance concentrations of either of the two or both (Odiyo and Makungo, 2018).

Table 9: Geothermal water/Groundwater quality within Soutpansberg and compliance to SABS (1999) and WHO (2004) drinking water standards.

Parameters	WHO Limit	SABS Limit	Measured parameters ranges	Compliance to guideline/s
pH	6.5-8.5	6-9	7.17-9.39	ALL except SAW and SH2
EC (µS/cm)	750	750	90-746.67	ALL
TDS (mg/L)	500	450	10.78-423.07	ALL
TH (mg/L)	100	NS	0.73-134.28	ALL except BH1 which is moderately hard
Ca (mg/L)	75	NS	0.29-27.80	ALL
Mg (mg/L)	30	NS	0.00-15.80	ALL
Na (mg/L)	200	200	1.69-170.00	ALL
K (mg/L)	100	50	1.06-5.15	ALL
F (mg/L)	1.5	1.0	0.00-6.51	NONE except SGW, SCC and TTP
Cl (mg/L)	250	200	3.73-156.67	ALL
NO_3 (mg/L)	10	NS	0.17-83.95	ALL except BH2
SO_4 (mg/L)	250	NS	0.48-51.78	ALL
HCO_3 (mg/L)	200	NS	2.44-98.75	ALL

NS – Not Stipulated, TH – Total Hardness

The hardness of water is attributed to the presence of alkaline earth metals, that is Ca^{2+} and Mg^{2+}, and they are very important property of water for domestic uses. Although, hardness has no known adverse effect on human health, it has an adverse effect on aesthetic property of the water, due to the unpleasant taste. Hardness has the following effects: prevent formation of lather with soap, increases the boiling point of water and causes encrustation in water supply distribution system

(Ako, 2011). Durvey *et al*. (1991) reported that long term consumption of extremely hard water might lead to an increased incidence of urolithiasis, anencephaly, perinatal mortality, cancer and cardiovascular disorder. In addition, high range of TH in water may cause corrosion in the pipe when certain trace metals are present (Garg *et al.,* 2009). Hardness of water is usually expressed as total hardness (TH) and is calculated by equation 4.6 (Todd, 1980)

$$TH = 2.5\ Ca + 4.1\ Mg \qquad \text{...14}$$

Where TH: total hardness as $CaCO_3$ in mg/l, Ca: Ca^{2+} concentration in mg/l, Mg: Mg^{2+} concentration in mg/l.

In this study, most of the water is classified to be soft except for TTP and BH1 that are moderately hard waters. Studies have shown that there is a link between TH and cardiovascular diseases. For instance, Dissanayake *et al*. (1992) reported a negative correlation between TH and leukemia and other cardiovascular disease in Siri-Lanka. Michael et al. (2016) reported hard water as an environmental trigger for eczema in children. Hence, soft waters are recommended because they can be helpful towards avoiding the irritation and improving certain health problems. Therefore, the hardness of these geothermal springs and boreholes were within the WHO recommendations except for BH1, which is moderately hard. Hence, they are suitable for domestic purposes due to their softness (based on these findings).

4.3.2 Irrigational purposes

The suitability of the geothermal water/groundwater for irrigation purposes is measured by several parameters. Tables 7 and 9 show these parameters; electrical conductivity (EC), sodium adsorption ratio (SAR), residual sodium carbonate (RSC), percentage sodium (SP), Kelly's ratio (KR), permeability index (PI) and Wilcox (US salinity) classification indices. Salinity is one of the major negative environmental impacts leading to loss of production, which is associated with irrigation. Salinity greatly affects crop germination and yield and can render the soil infertile. Hence, the need to assess the water quality for irrigation purposes because low quality irrigation waters could be suitable for sandy soil but hazardous to clayey soil and vice versa. Richard (1954) classified SAR and EC values for irrigation water into four categories: low ($EC \leq 250$ µS/cm, $SAR < 10$), medium (EC = 250-750 µS/cm, SAR= 10-18), high (EC = 750-2,250 µS/cm, SAR= 18-26) and very high (EC = 2,250-5, 000 µS/cm, $SAR > 26$). Ako (2011) reported that excessive solutes in irrigation water constitute a problem in semi-arid areas where water losses through evaporation is high. In this study, the geothermal water/groundwater has EC values ranging (90-746.67 μS/cm) and thus have low to medium salinity which makes them suitable for irrigation. Sodium percentage (SP) is a good parameter to assess the suitability of water for irrigation (Wilcox, 1958). High SP in soil causes impairment of tilth, deflocculating and permeability of soil. SP in geothermal water/groundwater was calculated using equation 15;

$$SP = (Na + K) / (Ca + Mg + Na + K) * 100 \quad \ldots\ldots 15$$

Pair (1983) reported that water with SP greater than 60% may result in sodium accumulations that will cause a breakdown in the soil's physical properties, hence, not suitable for irrigation. This implies that most of the samples from the study areas are not suitable for irrigation (SP> 60%) except for SCC and TTP (Table 10), which are treated.

Table 10: Index methods for groundwater suitability

SITES	CODES	RSC	PI	KR	SP
Sagole	SGW	10.97	104.39	221.38	99.56
	SGS	0.19	92.41	7.38	88.43
Tshipise	TSW	10.12	100.42	55.52	98.28
	TSS	9.71	100.42	55.38	98.28
	TTP	-16.37	45.27	0.6	40.13
Mphephu	MPW	-7.45	71.17	1.87	66.25
	MPS	14.93	69.75	1.9	66.65
Siloam	SAW	108.15	103.75	11.7	92.36
	SH1	6.81	99.5	33.43	97.16
	SH2	11.35	103.64	77.41	98.77
	BH1	-12.49	77.31	2.84	74.76
	BH2	2.4	93.28	10.29	91.36
	SCC	0.51	89.84	0.88	58.76

RSC - Residual sodium carbonate, PI - Permeability index, KR - Kelly's ratio, SP - Sodium percentage.

The sodium hazard is often expressed as SAR and is plotted against the conductance in a Wilcox diagram (Figure 16). Most of the geothermal water and boreholes are in C2S1 (medium salinity and low alkalinity) and C2S2 (medium salinity and medium alkalinity) fields which are suitable for irrigation. Siloam hot boreholes (SH1 and SH2) fall in C2S3 (medium salinity and high alkalinity) and Tshipise geothermal water (TSW and TSS) falls in (medium salinity and very high alkalinity), which implies that they are suitable for irrigation. On the contrary, similar studies in Andhra Pradesh (South India) and Yinchuan (China) showed that the majority of the groundwaters possess high salinity with low sodium (C3-S1) which are not suitable for irrigation (Nagaraju *et al*., 2014; Wu *et al*., 2015).

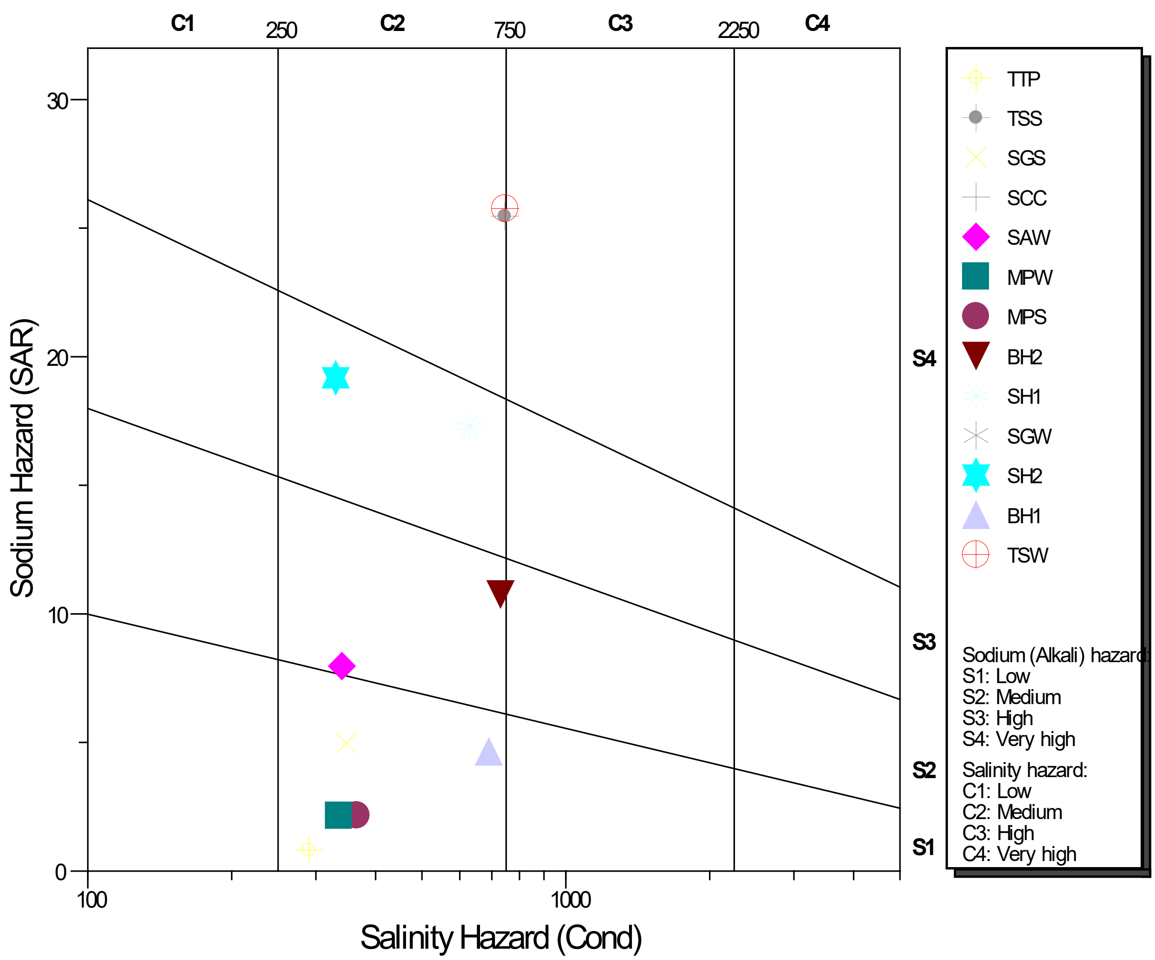


Figure 16*: Wilcox (US salinity) diagram of geothermal spring water/boreholes samples for winter and summer from the study areas.*

The water quality diminishes when the total carbonate levels exceed the amount of Ca^{2+} and Mg^{2+}. Hence, the residual sodium carbonate (RSC) index is calculated by equation 16 (Eaton 1950);

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \quad \text{……………….……………16}$$

The classification of irrigation water according to the RSC values is such that waters containing more than 2.5 meq/l of RSC are not suitable for irrigation, while those having 1 to 2.5 meq/l are marginal and those from 0-1 meq/l are good for irrigation (Eaton, 1950). Based on this classification, some of the water samples are not suitable for irrigation except for SGS, TTP, MPW SCC, BH1 that are good for irrigation and BH2 that has marginal quality for irrigation. The permeability index (PI) values also indicate the suitability of groundwater for irrigation and it is defined as follows (Equation 17):

$$PI=100*([Na^+] +\sqrt{[HCO_3^-]})/([Na^+] + [Ca^{2+}] + [Mg^{2+}] \quad \text{………….............17}$$

The World Health Organisation (WHO) (WHO, 1989) uses a criterion for assessing the suitability of water for irrigation based on PI. PI is classified under class I (>75%), class II (25-75%) and class III (<25%) orders, with class I and II good for irrigation. According to the PI values (Table 9), the geothermal water and borehole can be designated as class I and II and this implies that the water is good for irrigation (Aastri, 1994). Since there is little or no difference in the PI per season for different sites, the groundwater has no permeability and infiltration problems.

Kelly's ratio (KR) is computed by equation 18:

$$KR= Na^+ / (Ca^{2+} + Mg^{2+}) \quad \text{…………...………………………18}$$

The concentration of Na^+ measured against Ca^{2+} and Mg^{2+} is known as the Kelly's ratio (KR), based on which the quality of irrigation water can be assessed (Kelly, 1946). Kelly's ratio of water is categorised into suitable if KR is <1, marginal when KR is 1-2 and unsuitable if KR is >2 (Kelly, 1946). According to the classification, most of the geothermal water/groundwater were not suitable for irrigation except for TTP and SCC (Good), and MPW and MPS (Marginal). This corroborates with the sodium percentage (SP), which depicted that most of the samples in the studied sites are not suitable water for irrigation.

From the various indices employed in this study; SAR, PI, RSC and EC showed that most geothermal springs and about half of geothermal springs and boreholes are suitable for irrigation purposes except for KR and SP. According to Wilcox (US salinity) classification (which combines SAR and EC), the springs are suitable for irrigation. Hence, it can be recommended that most of the geothermal springs should be used for irrigation (Figure 16).

4.4 Trace metals concentrations from the geothermal springs and boreholes

Table 11 shows the mean values for trace metals concentrations in the geothermal springs, hot boreholes and tepid boreholes. Results show that geothermal springs are highly mineralised owing to their geological composition as supported by Todd (1980). More mineralisation of the geothermal springs was aided by the thermal gradient (temperature) leading to more mineral dissolution in water (Odiyo and Makungo, 2012). The obtained values were compared with the standard guidelines for drinking water by SANS (2015) and WHO (2004). Generally, the trace metals concentrations of the geothermal spring and boreholes within the Soutpansberg were within the drinking water permissible guidelines by the SABS and WHO, except for Mercury (Hg) which is high in summer (>1 µg/L). This high mercury concentration could be associated with igneous activity and circulating geothermal fluids that precipitate around geothermal springs, geysers and fumaroles, particularly during summer, when there is high rainfall (Barringer *et al.,* 2013). Though trace metals concentrations were within the drinking water guidelines, the accumulation in the human body could result in adverse effect considering that some of these metals are carcinogenic in nature.

Generally, the mean trace metals concentrations were higher in summer compared to winter except for some trace metals such as Be, Ni, Cu, Zn, Se, Ba at different sites with anomalous concentrations. This could be attributed to the temperature differences and more rainfall leading to more dissolution of the host rock (minerals) in summer.

The mean trace metals concentrations within the study areas were in relatively good agreement during summer for geothermal springs (Table 11). As stated earlier, more rainfall in summer (wet) enhances more rock-water interaction at the deep aquifer of the geothermal spring and more trace metals were released into the water body at the surface. Therefore, there are more trace metals in the geothermal spring water during summer (wet) than in the winter (dry). At Siloam, anomalous trend was found among the geothermal spring, hot borehole and tepid boreholes, where the boreholes were in some cases more enriched with trace metals than the geothermal spring. This could possibly be linked to the geology of the area, although, the geology of an area is complex and differs from one point to another (Olivier *et al*., 2008; 2011). For instance, two houses where the borehole water was sampled are next to one another and their water characteristics are different (one is hot and the other is cold). Hence, there is possibility of common host rock and minor faults connecting the aquifer of geothermal spring and boreholes.

Relationships of trace metals in water with some physicochemical parameters were evaluated using the Pearson's test (Table 12). There is a direct relationship between temperature and alkalinity, pH, EC, V, Zn, Hg and Pb. This means that an increase in water temperature results to increase in EC, pH (leading to high alkalinity) and trace metals such as V, Zn, Hg, Pb. This is an indication of dissolution of minerals (rock-water interaction) under high temperature. Also, there was a negative correlation between temperature and other trace metals (Be, Cr, Mn, Co, Ni, Cu, As, Se, Cd, Sb, Ba). This means that these trace metals are in good agreement with one another or perhaps have some common minerals in their compositions. This study revealed that pH has a negative correlation with all the trace metals (Be, Cr, Mn, Co, Ni, Cu, As, Se, Cd, Sb, Ba, V, Zn, Hg) except Pb. This means that increase in pH (basic) results to decrease in trace metals concentrations in the geothermal springs/boreholes; which shows that there is less indication of trace metals pollution (insoluble) (EPA, 1987). This is in support of a previous study that stated that most metals seem to be more toxic in acidic state (Witeska and Jezierska, 2003). The conductivity values had a significant positive relationship with all trace metals such as Be, V, Mn, Co, Ni, Cu, Zn, Cd, Sb, Ba, Hg, Pb except alkalinity, Cr, As and Se. It could be inferred that the changes of physicochemical parameters depend on how seasons affect the levels of some metals (Radulescu *et al.,* 2014).

The relationships among the trace metals were further determined by hierarchical cluster analysis (HCA) using XLSTAT statistical software (Shan et al., 2012). They were grouped into clusters based on the similarities and dissimilarities between different metals (Figure 17). Dendrogram analysis produced 6 clusters for the spatial distribution of trace metals of the samples; clusters 2 and 5 include pH and all the trace metals except Cu. These metals are likely present in the geothermal springs/boreholes due to agricultural run-off or atmospheric deposition in the study areas (Iqbal and Shah, 2013). This corroborated by the findings from the Pearson correlation matrix; trace metals are insoluble at higher pH (basic medium), hence the negative correlation. Clusters 1, 3, 4, and 6 are temperature, conductivity, alkalinity and Cu, respectively, occurred independently. The results of cluster analysis supported the correlation results, which suggested that the selected metals are from anthropogenic and natural sources.

Table 11: Mean trace metal concentrations of the geothermal springs and boreholes within Soutpansberg

	SABS; WHO	TSS	TSW	SGS	SGW	MPS	MPW	SAW	SH1	SH2	BH1	BH2	SCC	TTP
Temp(°C)		55.4.	54.60	44.80	42.40	42.70	41.30	67.70	45.20	48.40	22.40	21.40	20.10	22.50
pH	6-9	8.47	8.46	7.98	8.82	8.15	8.05	9.39	8.86	9.19	8.17	8.1	7.17	8.17
EC	<750	745.00	746.67	347.33	330.00	365.00	335.00	340.00	630.00	330.00	690.00	730.00	90.00	290.00
Alkalinity		10.75	11.12	6.5	10.50	6.00	12.5	107.52	10.00	12.00	25.50	17.50	2.00	11.50
Be (µg/l)		1.83	5.84	1.34	0.01	2.60	5.13	0.05	3.21	3.53	4.37	6.76	5.06	0.01
V (µg/l)		18.36	16.74	13.51	14.59	16.28	13.96	3.21	13.54	17.63	5.12	12.46	17.83	4.62
Cr (µg/l)	50; 100	12.46	8.64	10.48	6.64	10.57	8.40	0.09	10.40	11.08	6.99	6.48	12.14	9.03
Mn (µg/l)	500; 1000	2.67	2.22	10.30	25.55	36.60	1.06	0.24	1.25	1.95	107.50	1.66	1.52	14.69
Co (µg/l)		0.21	0.28	0.43	0.36	0.29	0.36	0.04	0.19	0.26	3.42	0.51	0.24	0.17
Ni (µg/l)	20; 150	2.25	2.64	0.99	1.11	2.14	0.84	0.71	0.82	1.48	12.52	0.55	1.88	1.57
Cu (µg/l)	2000; 1000	11.97	18.75	30.58	0.06	1.28	0.01	0.35	0.01	1.84	31.39	0.34	2.15	4.82
Zn (µg/l)	3000; 5000	312.90	464.85	294.38	194.59	49.35	21.00	0.95	0.01	0.01	350.90	0.01	0.01	44.86
As (µg/l)	10; 10	2.04	2.01	1.35	1.97	2.72	2.10	1.01	1.03	3.04	1.92	1.29	3.05	1.30
Se (µg/l)		5.83	6.18	3.86	5.74	10.02	6.42	0.68	5.07	10.95	5.85	3.62	10.94	3.25
Cd (µg/l)		0.06	0.02	0.01	0.05	0.01	0.14	0.02	0.01	0.01	0.73	0.01	0.01	0.05
Sb (µg/l)	5; 5	0.05	0.02	0.03	0.06	0.04	0.17	0.03	0.01	0.02	0.12	0.08	0.01	0.10
Ba (µg/l)		1.54	26.39	0.78	42.39	8.79	29.00	10.42	0.38	7.20	67.32	71.98	6.84	0.01
Hg (µg/l)	1; 1	**6.11**	0.62	**3.26**	0.40	**1.82**	0.43	0.35	0.66	0.80	0.15	**1.60**	0.46	0.72
Pb (µg/l)	10; 20	0.28	0.33	0.49	0.01	0.01	0.01	0.09	0.17	0.01	0.01	0.01	0.01	0.06

Table 12: Pearson correlation matrix showing the relationships between trace metals and physicochemical parameters in geothermal springs and boreholes water

Variables	Temp	pH	EC	Alk	Be	V	Cr	Mn	Co	Ni	Cu	Zn	As	Se	Cd	Sb	Ba	Hg	Pb
Temp	**1.00**																		
pH	**0.71**	**1.00**																	
EC	0.13	0.21	**1.00**																
Alkalinity	0.48	**0.55**	-0.04	**1.00**															
Be	-0.36	-0.42	0.37	-0.33	**1.00**														
V	0.13	-0.22	0.02	**-0.65**	0.37	**1.00**													
Cr	-0.25	-0.48	-0.04	**-0.86**	0.22	**0.72**	**1.00**												
Mn	-0.38	-0.13	0.20	-0.03	0.00	-0.40	-0.12	**1.00**											
Co	-0.42	-0.17	0.34	0.00	0.23	-0.39	-0.13	**0.93**	**1.00**										
Ni	-0.34	-0.16	0.34	0.00	0.19	-0.34	-0.05	**0.92**	**0.96**	**1.00**									
Cu	-0.06	-0.23	0.35	-0.12	0.05	-0.15	0.12	0.54	**0.63**	**0.64**	**1.00**								
Zn	0.18	-0.06	0.53	-0.18	0.03	0.10	0.11	0.38	0.41	0.49	**0.81**	**1.00**							
As	-0.14	-0.30	-0.35	-0.44	0.30	**0.64**	0.54	0.08	0.02	0.12	-0.11	-0.03	**1.00**						
Se	-0.21	-0.32	-0.29	**-0.58**	0.37	**0.70**	**0.68**	0.06	0.00	0.09	-0.15	-0.11	**0.95**	**1.00**					
Cd	-0.35	-0.12	0.30	0.06	0.17	-0.44	-0.17	**0.90**	**0.98**	**0.96**	**0.58**	0.39	0.00	-0.04	**1.00**				
Sb	-0.36	-0.24	0.09	-0.04	0.15	-0.37	-0.21	0.37	0.44	0.34	0.09	0.03	-0.13	-0.22	0.54	**1.00**			
Ba	-0.42	-0.10	0.43	0.03	0.48	-0.22	-0.41	0.51	**0.62**	0.48	0.16	0.19	-0.09	-0.15	**0.57**	0.51	**1.00**		
Hg	0.26	-0.09	0.33	-0.21	-0.18	0.38	0.44	-0.19	-0.20	-0.15	0.26	0.33	-0.02	-0.05	-0.21	-0.13	-0.30	**1.00**	
Pb	0.43	0.00	0.30	-0.10	-0.15	0.19	0.23	-0.26	-0.19	-0.15	**0.60**	**0.61**	-0.34	-0.31	-0.22	-0.34	-0.39	**0.56**	**1.00**

Values in bold are different from 0 with a significance level alpha=0.05, Alk - Alkalinity

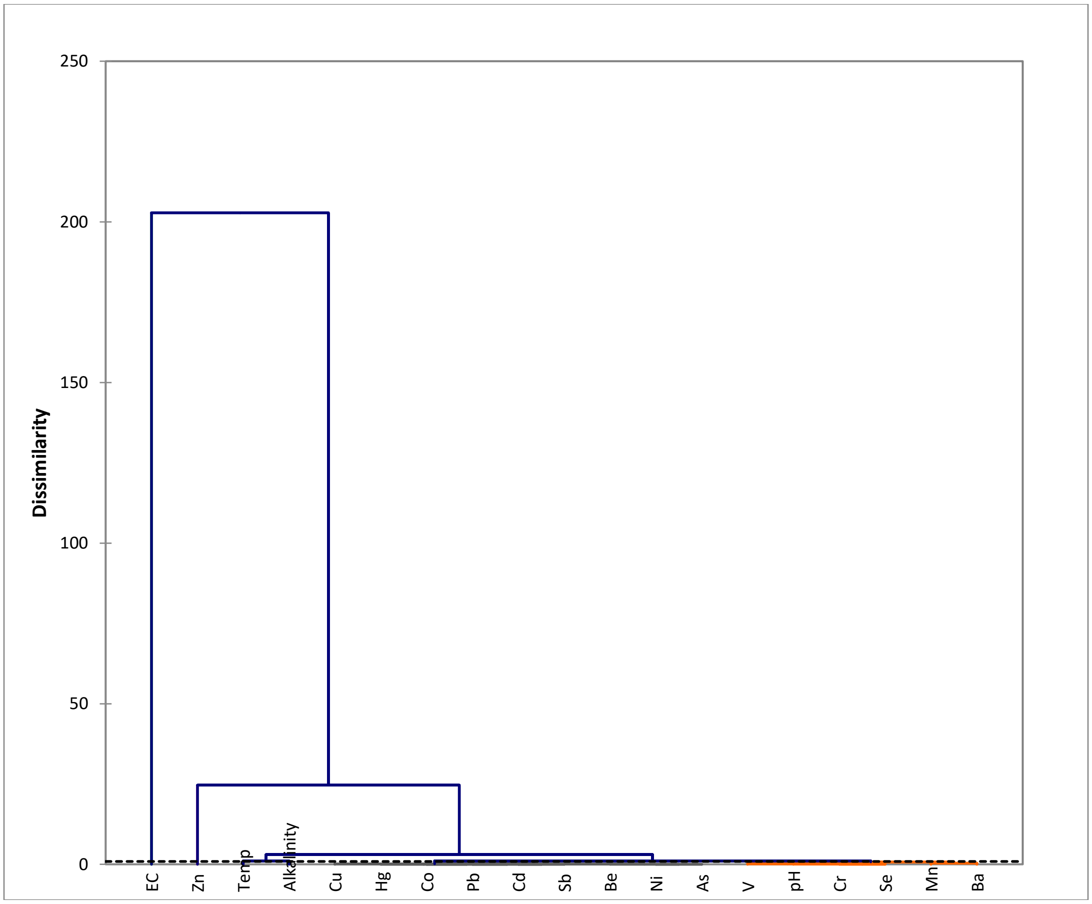


Figure 17: *Dendrogram showing the spatial clustering of trace metals in geothermal spring/borehole water samples based on the hierarchical cluster analysis using Ward's method*

The PCA/FA loading factors for the trace metals in the geothermal springs/borehole samples taken within Soutpansberg are shown in Table 13. For both seasons (winter and summer), five important principal components (PCs) were significant with eigenvalues > 1, explaining higher total variance of 30.27, 53.20, 70.59, 79.00 and 86.61% respectively (Table 12 and Figure 16). The factor loadings show that F1 (30.27%) has high loadings of Mn, Co, Ni, Cu, Cd, Sb, Ba; F2 (22.93%) with high loadings of V, Cr, As, Se; F3 (17.39%) with high loading of EC, Cu, Zn, Hg, Pb; F4 (8.42%) with the highest loading of Be; F5 (7.60%) with high loadings of pH. Multivariate analysis using PCA/FA is very useful as a monitoring tool to identify the multiple sources of contaminants and relationships with trace metals in the groundwater (Figure 18). The five factors are interrelated and are indicative of rock-water interaction, such as thermal gradient, mineral dissolution and ion exchange as the major geochemical processes governing the groundwater chemistry. This supports the previous findings in water types and confirms that the rock-water interaction is one of the major processes controlling the chemistry of the geothermal spring and boreholes.

Table 13: Factor loadings of the trace metals concentrations and some physicochemical parameters

	F1	F2	F3	F4	F5
Temperature	-0.4432	-0.4625	0.4421	-0.2965	0.4432
pH	-0.1900	-0.6551	0.0840	-0.2828	**0.5248**
EC	0.3886	-0.0839	**0.5363**	0.4553	0.4652
Alkalinity	0.0419	-0.8558	-0.1334	-0.1990	0.1804
Be	0.2417	**0.5150**	-0.1384	**0.5436**	0.4214
V	-0.4874	**0.7351**	0.2189	0.0749	0.3380
Cr	-0.2476	**0.8574**	0.2698	-0.0474	-0.1765
Mn	**0.8936**	0.0911	-0.0276	-0.3416	-0.0365
Co	**0.9687**	0.0988	0.0185	-0.1507	0.0416
Ni	**0.9219**	0.1502	0.0891	-0.2885	0.0746
Cu	**0.6030**	0.1119	**0.6812**	-0.1419	-0.1886
Zn	0.4386	0.1176	**0.7799**	-0.0682	0.1081
As	-0.1061	**0.7733**	-0.2425	-0.4112	0.2689
Se	-0.1487	**0.8540**	-0.2373	-0.3470	0.2594
Cd	**0.9591**	0.0341	-0.0101	-0.1859	0.0197
Sb	**0.5607**	-0.0521	-0.2696	0.3223	-0.2290
Ba	**0.7120**	-0.0234	-0.2423	0.4370	0.3215
Hg	-0.2335	0.1716	**0.6983**	0.0980	-0.1280
Pb	-0.1928	-0.0659	**0.9167**	0.0710	-0.1803
Eigenvalue	5.7517	4.3560	3.3038	1.5992	1.4443
Variability (%)	30.2721	22.9262	17.3885	8.4166	7.6015
Cumulative (%)	**30.2721**	**53.1983**	**70.5868**	**79.0034**	**86.6050**

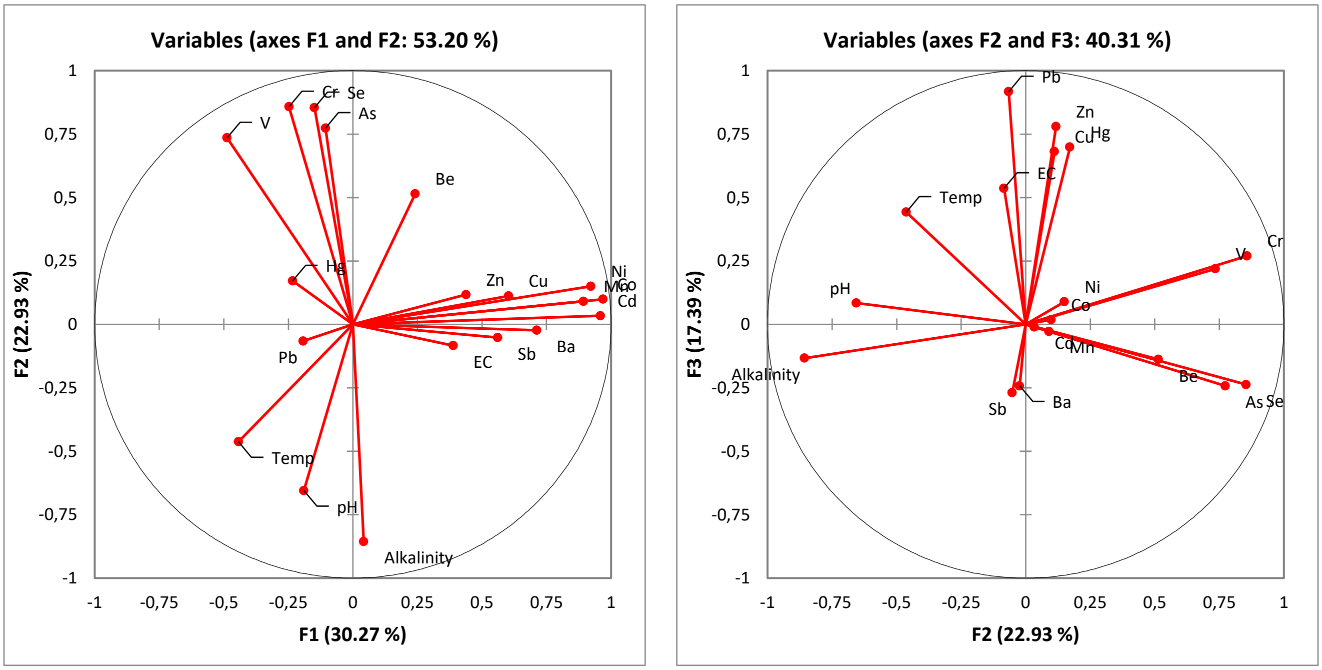


***Figure 18**: The principal component analysis (PCA) biplots showing the relationships between trace metals in the geothermal spring and borehole samples*

4.4.1 Evaluation of human health risk associated with trace metals in geothermal springs/boreholes

The level of exposure through ingestion and dermal contact were estimated since these are the major exposure pathways of geothermal springs and boreholes in the communities. Possible health risk associated with the exposure through ingestion depends on the weight, age and volume of groundwater consumed by an individual (children and adults) as presented in Table 14. In most of the study areas, the children's chronic daily intake was higher than the adults, indicating that children are more susceptible to potential health risk associated with the consumption of trace metals. When hazard quotient (HQ) and hazard index (HI) are less than one, there is no obvious risk to the population, but if these values exceed one, there may be concern for potential non-carcinogenic effects (Naveedullah *et al.,* 2014; Asare-Donkor *et al.,* 2016). The calculated cumulative hazard quotients (HI) for all the trace metals served as a conservative assessment tool to estimate high-end risk rather than low end-risk in order to protect the public. Calculated HI served as a screen value to determine whether there is a major significant health risk that exposure of trace metals in the groundwater may pose on the community and if there is any difference in total health risk during the study period. For the adult population, the calculated values for HQ were less than one in dermal intakes (Appendix 1). Although, calculated HI (summation of the HIs) for all the exposure pathways was 1.23, a value greater than one is due to the ingestion pathways. Trace metals such as Be, Cr, Hg and As are the main drivers (HI values ranges from 0.1-0.5), hence, the adult population was at risk of non-carcinogenic diseases.

For children, calculated HI (summation of the HIs) was 54.7 with Be, Se, As, Mn, Cr, Hg and V (Appendix 1) being the major drivers (HI values ranges from 1.04-9.94), through ingestion pathway. This high value indicated trace metal pollution that may pose a very high non-cancer health risk to children living in those communities. In general, health risk assessment index using the overall non-carcinogenic risk assessment (HI), CDI and HQ via ingestion and dermal adsorption routes were greater than one. This is an indication that groundwater poses more significant health threats to both adults and children via the pathways (Asare_Donkor et al., 2016; Naveedullah et al. 2014), however measures should be made to avoid accumulation of heavy metals that pose adverse health problems especially in children.

The carcinogenic risk of only Cr, Cd, As and Pb were calculated for both adults and children because the values of carcinogenic slope factors for the other trace metals could not be found in literature. According to regulatory bodies the carcinogenic risk values between 10^{-6} and 10^{-4} for an individual suggest a potential risk (USEPA, 2004; Government of South Africa, 2006). In this study, Cr, Cd and As were found to be the highest contributors to the cancer risk in adults and children, respectively (Table 15). Pb poses carcinogenic risk to children in all the sites in both seasons and this is of great concern and requires attention. Whereas Cd also poses cancer risk in children at all sites but fall within the acceptable limit for adult population except for MPW and BH1. Hence, Cd poses cancer risk in adult at MPW and BH1. SAW (Siloam) having 4.04E-05 in Cr, also does not poses a cancer risk to its population unlike other sites. Therefore, proper monitoring and control measures to protect human health within the study areas should be implemented for safety.

Table 14: Average chronic daily intake (CDI) values in mg/kg/day of geothermal water/boreholes for adults and children within Soutpansberg

		TSS	TSW	SGS	SGW	MPS	MPW	SAW	SH1	SH2	BH1	BH2	SCC	TTP
Be	Children	2.19E-01	7.01E-01	1.61E-01	1.08E-03	3.12E-01	6.16E-01	6.00E-03	3.85E-01	4.23E-01	5.24E-01	8.11E-01	6.07E-01	1.08E-03
	Adult	5.74E-02	1.83E-01	4.21E-02	2.83E-04	8.16E-02	1.61E-01	1.57E-03	1.01E-01	1.11E-01	1.37E-01	2.13E-01	1.59E-01	2.83E-04
V	Children	2.20E+00	2.01E+00	1.62E+00	1.75E+00	1.95E+00	1.68E+00	3.85E-01	1.62E+00	2.12E+00	6.14E-01	1.50E+00	2.14E+00	5.54E-01
	Adult	5.77E-01	5.26E-01	4.25E-01	4.59E-01	5.12E-01	4.39E-01	1.01E-01	4.26E-01	5.54E-01	1.61E-01	3.92E-01	5.60E-01	1.45E-01
Cr	Children	1.50E+00	1.04E+00	1.26E+00	7.97E-01	1.27E+00	1.01E+00	1.08E-02	1.25E+00	1.33E+00	8.39E-01	7.78E-01	1.46E+00	1.08E+00
	Adult	3.92E-01	2.71E-01	3.29E-01	2.09E-01	3.32E-01	2.64E-01	2.83E-03	3.27E-01	3.48E-01	2.20E-01	2.04E-01	3.82E-01	2.84E-01
Mn	Children	3.20E-01	2.67E-01	1.24E+00	3.07E+00	4.39E+00	1.28E-01	2.88E-02	1.50E-01	2.34E-01	1.29E+01	1.99E-01	1.83E-01	1.76E+00
	Adult	8.38E-02	6.99E-02	3.24E-01	8.03E-01	1.15E+00	3.35E-02	7.54E-03	3.94E-02	6.12E-02	3.38E+00	5.20E-02	4.79E-02	4.62E-01
Co	Children	2.51E-02	3.34E-02	5.18E-02	4.27E-02	3.49E-02	4.37E-02	4.80E-03	2.23E-02	3.13E-02	4.11E-01	6.10E-02	2.86E-02	2.04E-02
	Adult	6.58E-03	8.75E-03	1.36E-02	1.12E-02	9.15E-03	1.15E-02	1.26E-03	5.85E-03	8.20E-03	1.08E-01	1.60E-02	7.48E-03	5.34E-03
Ni	Children	2.69E-01	3.16E-01	1.19E-01	1.33E-01	2.56E-01	1.01E-01	8.52E-02	9.80E-02	1.78E-01	1.50E+00	6.54E-02	2.26E-01	1.89E-01
	Adult	7.06E-02	8.28E-02	3.12E-02	3.47E-02	6.72E-02	2.65E-02	2.23E-02	2.57E-02	4.66E-02	3.93E-01	1.71E-02	5.92E-02	4.94E-02
Cu	Children	1.44E+00	2.25E+00	3.67E+00	7.70E-03	1.54E-01	1.08E-03	4.20E-02	1.08E-03	2.21E-01	3.77E+00	4.13E-02	2.58E-01	5.78E-01
	Adult	3.76E-01	5.89E-01	9.61E-01	2.02E-03	4.02E-02	2.83E-04	1.10E-02	2.83E-04	5.78E-02	9.87E-01	1.08E-02	6.76E-02	1.51E-01
Zn	Children	3.75E+01	5.58E+01	3.53E+01	2.34E+01	5.92E+00	2.52E+00	1.14E-01	1.08E-03	1.08E-03	4.21E+01	1.08E-03	1.08E-03	5.38E+00
	Adult	9.83E+00	1.46E+01	9.25E+00	6.12E+00	1.55E+00	6.60E-01	2.99E-02	2.83E-04	2.83E-04	1.10E+01	2.83E-04	2.83E-04	1.41E+00
As	Children	2.45E-01	2.42E-01	1.62E-01	2.37E-01	3.27E-01	2.52E-01	1.21E-01	1.24E-01	3.65E-01	2.30E-01	1.55E-01	3.66E-01	1.56E-01
	Adult	6.42E-02	6.33E-02	4.25E-02	6.20E-02	8.55E-02	6.59E-02	3.17E-02	3.24E-02	9.56E-02	6.03E-02	4.07E-02	9.59E-02	4.09E-02
Se	Children	6.99E-01	7.42E-01	4.63E-01	6.89E-01	1.20E+00	7.70E-01	8.16E-02	6.08E-01	1.31E+00	7.02E-01	4.34E-01	1.31E+00	3.90E-01
	Adult	1.83E-01	1.94E-01	1.21E-01	1.80E-01	3.15E-01	2.02E-01	2.14E-02	1.59E-01	3.44E-01	1.84E-01	1.14E-01	3.44E-01	1.02E-01
Cd	Children	6.76E-03	2.94E-03	1.60E-03	6.46E-03	9.20E-04	1.65E-02	2.40E-03	1.08E-03	8.40E-04	8.71E-02	1.08E-03	8.40E-04	5.40E-03
	Adult	1.77E-03	7.70E-04	4.19E-04	1.69E-03	2.41E-04	4.32E-03	6.29E-04	2.83E-04	2.20E-04	2.28E-02	2.83E-04	2.20E-04	1.41E-03
Sb	Children	6.36E-03	2.64E-03	3.76E-03	7.06E-03	4.28E-03	2.07E-02	3.60E-03	6.00E-04	1.80E-03	1.46E-02	9.48E-03	1.08E-03	1.14E-02
	Adult	1.67E-03	6.91E-04	9.85E-04	1.85E-03	1.12E-03	5.42E-03	9.43E-04	1.57E-04	4.71E-04	3.83E-03	2.48E-03	2.83E-04	2.99E-03
Ba	Children	1.84E-01	3.17E+00	9.36E-02	5.09E+00	1.06E+00	3.48E+00	1.25E+00	4.55E-02	8.64E-01	8.08E+00	8.64E+00	8.21E-01	1.08E-03
	Adult	4.83E-02	8.29E-01	2.45E-02	1.33E+00	2.76E-01	9.11E-01	3.27E-01	1.19E-02	2.26E-01	2.12E+00	2.26E+00	2.15E-01	2.83E-04
Hg	Children	7.33E-01	7.45E-02	3.91E-01	4.83E-02	2.18E-01	5.17E-02	4.20E-02	7.94E-02	9.58E-02	1.84E-02	1.92E-01	5.52E-02	8.64E-02
	Adult	1.92E-01	1.95E-02	1.02E-01	1.27E-02	5.71E-02	1.35E-02	1.10E-02	2.08E-02	2.51E-02	4.81E-03	5.03E-02	1.45E-02	2.26E-02
Pb	Children	3.38E-02	3.91E-02	5.87E-02	1.08E-03	1.08E-03	1.08E-03	1.08E-02	2.05E-02	1.08E-03	1.08E-03	1.08E-03	1.08E-03	7.68E-03
	Adult	8.86E-03	1.02E-02	1.54E-02	2.83E-04	2.83E-04	2.83E-04	2.83E-03	5.37E-03	2.83E-04	2.83E-04	2.83E-04	2.83E-04	2.01E-03

Table 15: Carcinogenic risk assessment of Cr, Cd, As and Pb from geothermal springs/boreholes within Soutpansberg through ingestion pathway for adults and children

	Cr		Cd		As		Pb	
Code	Children	Adults	Children	Adults	Children	Adults	Children	Adults
TSS	2.49E-01	5.59E-03	4.26E-02	9.56E-04	1.22E+00	2.71E-02	8.22E-05	5.84E-08
TSW	1.73E-01	3.88E-03	1.85E-02	4.16E-04	1.21E+00	1.82E-02	9.50E-05	6.75E-08
SGS	2.10E-01	4.70E-03	1.01E-02	2.26E-04	8.12E-01	2.66E-02	1.43E-04	1.01E-07
SGW	1.33E-01	2.98E-03	4.07E-02	9.13E-04	1.18E+00	3.67E-02	2.62E-06	1.86E-09
MPS	2.11E-01	4.75E-03	5.80E-03	1.30E-04	1.63E+00	2.82E-02	2.62E-06	1.86E-09
MPW	1.68E-01	3.77E-03	1.04E-01	2.33E-03	1.26E+00	1.36E-02	2.62E-06	1.86E-09
SAW	1.80E-03	4.04E-05	1.51E-02	3.39E-04	6.06E-01	1.39E-02	2.62E-05	1.86E-08
SH1	2.08E-01	4.67E-03	6.80E-03	1.53E-04	6.19E-01	4.10E-02	4.98E-05	3.54E-08
SH2	2.22E-01	4.97E-03	5.29E-03	1.19E-04	1.83E+00	2.59E-02	2.62E-06	1.86E-09
BH1	1.40E-01	3.14E-03	5.49E-01	1.23E-02	1.15E+00	1.74E-02	2.62E-06	1.86E-09
BH2	1.30E-01	2.91E-03	6.80E-03	1.53E-04	7.76E-01	4.11E-02	2.62E-06	1.86E-09
SCC	2.43E-01	5.45E-03	5.29E-03	1.19E-04	1.83E+00	1.75E-02	2.62E-06	1.86E-09
TTP	1.81E-01	4.05E-03	3.40E-02	7.64E-04	7.80E-01	3.35E-01	1.87E-05	1.32E-08

4.5 Trace metals concentrations from surrounding soils

The surrounding soils were sampled vertically from a depth of 10 cm, 30 cm and 50 cm and mean values of trace metals concentrations are presented in Table 16 and descriptive statistics are included in Appendix 2 for both seasons. Although, depths of 10 cm and 30 cm were used for sampling soil at Mphephu and Siloam owing to the nature of their soils (rocky soil), the concentrations of the trace metals varied from different sampling points at different site. At Sagole, the coefficient of variation of some trace metals such as As, Sb, Ba and Hg were 151.66, 141.51, 159.91 and 139.94 for summer, respectively, and 161.66 of Hg in winter (Appendix 2). These high coefficients of variations suggest anthropogenic inputs as their main source. Most of the trace metals were within acceptable limits (Department of Environmental Affairs, 2010) except for Cu at Siloam and Mphephu soils, and at sampling depth W50 in Tshipise; Cr at all the sites except for Sagole (S30, S50 and W50); As at Sagole (S50) and Pb in Siloam (S10 and S30) (Table 16). Hence, the soils in the sites where the trace metals concentrations exceed the standards are contaminated. Generally, the pH ranges from acidic to alkaline and this account for the solubility of the trace metals in soil. The pH varied from 7.5 to 8.55, 3.1 to 9.9, 6.62 to 6.97 for summer at Tshipise, Sagole and Mphephu, respectively. Whereas pH varied from 8.01 to 8.05, 9.31 to 9.72, 7.47 to 7.76 for winter at Tshipise, Sagole and Mphephu, respectively. Siloam sampling points have pH, which ranges from 6.67 to 7.15. The slightly acidic and slightly alkaline nature of the soil in the study sites, for example at Mphephu and Siloam enhances the solubility of trace metals (Witeska and Jezierska, 2003).

Generally, trace metals concentrations are comparable in both seasons, though in some cases the concentrations at given depths in each of the sites are higher either in summer or winter. Though one would have expected the deeper depths of the soil to be more enriched with trace metals than the top surface of the soil due to leaching from the top soil to the bottom soil, the complexity of the soil environment and the source or location of the trace metal and their solubility makes this convoluted. The soil at Siloam was the most enriching in trace metals and to some extent Mphephu soils and this was due to the clayey nature of the soil. Though, the soil was loosely packed with rocky materials, its clayey texture (implying high retention capacity) accounts for higher trace metal concentrations than others. The soil types are sandy, sand loamy and clay loamy for Sagole, Tshipise and Mphephu soils, respectively (Olivier *et al*., 2008; Durowoju, 2015). Therefore, based on the retention capacity of the soil (soil type), the average magnitude of the absorbed trace metals was in this order of sequence; Siloam > Mphephu > Tshipise > Sagole.

Pearson correlation shows the relationship between trace metals concentrations and physicochemical parameters (Table 17). The pH values showed a negative correlation with all the trace metals except for Hg and Mn (very weak positive correlation). This means that the higher the pH of the soil, the lesser the trace metals concentrations in soil and vice versa. Invariably, this relationship justifies the fact that trace metals are more soluble in acidic soils and tend to be insoluble in alkaline soil. Very strong negative correlation was observed between the pH and trace metals Be, As, Sb and Ba. EC and TDS showed a positive correlation with Be, As, Sb, Ba and Hg. This is an indication of similar source. Generally, most of the trace metals had positive correlations with each other.

Table 16: Mean concentrations of the trace metals from the surrounding soil of the geothermal springs

		Tshipise (mg/Kg)						Sagole (mg/Kg)						Siloam (mg/Kg)		Mphephu (mg/Kg)			
	DEA, 2010	S10	S30	S50	W10	W30	W50	S10	S30	S50	W10	W30	W50	S10	S30	S10	S30	W10	W30
pH		7.5	8.55	8.32	8.05	8.05	8.01	9.9	9.14	3.1	9.72	9.33	9.31	7.15	6.67	6.62	6.97	7.76	7.47
EC		154.2	89.4	253.9	95.8	90.1	130.2	1441	124.1	973	376	253.7	195.8	90.6	116.9	217.5	111.2	27.4	40.8
TDS		98.7	57.2	162	613	57.6	83.3	922	79.4	623	241	162	125	58	74.8	139	71.1	17.5	26.1
Be	-	0.188	0.138	0.212	0.226	0.214	0.299	0.11	0.05	0.754	0.093	0.058	0.04	0.588	0.643	0.626	0.337	0.198	0.312
V	150	17.13	12.24	16.39	18.27	16.82	25.23	6.864	4.152	7.016	6.534	5.381	4.134	165.1	172.4	68.17	58.5	49.02	48.14
Cr	6.5	**46.23**	**37.93**	**42.85**	**37.5**	**36.93**	**44.9**	**9.977**	3.765	4.493	**7.81**	**7.267**	4.707	**90.54**	**96.35**	**36.1**	**35.32**	**27.92**	**38.38**
Mn	740	113.2	99.98	144	130.3	120.3	157.1	68.76	18.07	33.11	53.96	30.15	24.59	118.3	119	35.41	47.22	46.96	71.84
Co	300	5.084	3.623	5.284	4.96	4.61	7.781	2.293	0.888	2.124	1.518	1.117	0.999	28.66	28.67	14.66	13.8	19.12	21.52
Ni	91	34.44	24.46	31.59	26.1	26.84	37.03	11.27	2.414	4.311	6.13	4.439	3.405	51.65	57.39	21.1	15.72	11.6	21.45
Cu	16	12.7	8.519	12.16	13.73	15.05	**19.13**	8.687	8.108	9.229	7.141	5.796	5.628	**97.07**	**103.6**	**33.45**	**25.09**	**19.3**	**25.39**
Zn	240	15.24	14.16	15.75	16.15	15.49	21.25	17.17	10.64	2.512	4.93	3.827	6.104	48.62	48.94	37.74	15.52	8.082	19.77
As	5.8	0.382	0.222	0.309	0.369	0.673	0.925	0.333	0.337	**7.41**	0.587	0.263	0.326	0.787	0.794	1.098	0.435	0.103	0.668
Se	-	0.27	0.092	0.091	0.177	0.182	0.18	0.07	0.14	0.093	0.098	0.083	0.001	0.264	0.252	1.534	0.36	0.114	0.332
Cd	7.5	0.034	0.043	0.024	0.024	0.028	0.035	0.022	0.01	0.012	0.01	0.006	0.017	0.257	0.357	0.094	0.04	0.018	0.037
Sb	-	0.014	0.017	0.013	0.021	0.037	0.033	0.019	0.022	0.295	0.02	0.012	0.012	0.029	0.022	0.037	0.017	0.01	0.013
Ba	-	12.29	11.09	13.88	14.51	16.23	20.81	10.54	3.169	253.2	19.87	5.69	3.437	48.4	51.48	45.36	23.8	18.03	41.58
Hg	0.93	0.229	0.15	0.105	0.066	0.291	0.025	0.118	0.001	0.017	0.001	0.043	0.001	0.001	0.001	0.005	0.001	0.001	0.001
Pb	20	2.358	1.996	2.417	2.959	3.89	5.742	6.084	1.74	1.425	1.486	1.148	1.153	**85.02**	**30.6**	9.453	4.078	2.963	3.51

S10-S50 (depth of 10-50 cm at the four sites for summer; W10-W50 (depth of 10-50 cm at the four sites for winter)

The relationships among the trace metals were further determined using a dendrogram (HCA) (Figure 19). Dendrogram analysis produced 5 clusters for the spatial distribution of trace metals of the soil samples; Cluster 1 has pH, Be, As, Se, Cd, Se and Hg; Cluster 4 has V, Cr, Co, Ni, Cu, Ba and Pb; and EC, TDS and Mn are independent clusters 2, 3 and 5, respectively. The dendrogram further strengthens the relationship observed by Pearson's correlation by revealing the major clusters (1 and 4).

The PCA/FA loadings for the trace metals in the surrounding soil samples taken within study sites are shown in Table 18. Three principal components (PCs) were significant with eigenvalues > 1, explaining higher total cumulative variance of 80.78% (Table 17 and Figure 18). The factor loadings show that F1 (44.24%) has high loadings of V, Cr, Co, Cu, Zn, Be, Cd, Pb and Ni; F2 (26.16%) with the high loadings of EC, As, Sb and Ba: F3 (10.37%) with the high loadings of Mn, As and Hg. F1 could be attributed to soil pedogenesis. Soil contains trace quantities of these elements based on its parent material and soil forming factors (soil pedogenesis) (Siegel, 2002). F2 could be attributed to groundwater-surface soil interaction in which the soil absorbs trace elements resulting in their accumulation (Lakshmanan et al., 2003). Geothermal water and groundwater are used for irrigation purposes at all the sites and there is a high tendency of the trace elements mobility to the soil surface. The EC and TDS in the F2 are useful indicators which show the solubility of the trace metals from the groundwater into the surrounding soil, which, bioaccumulate with time (Durowoju *et al*., 2016b). F3 suggests anthropogenic source such as wastewater discharges and sewage sludge around the study sites. The pH has direct relationship with trace metals from the varimax (Figure 20) and is also indicative of anthropogenic activities leading to the release of Hg to the soil.

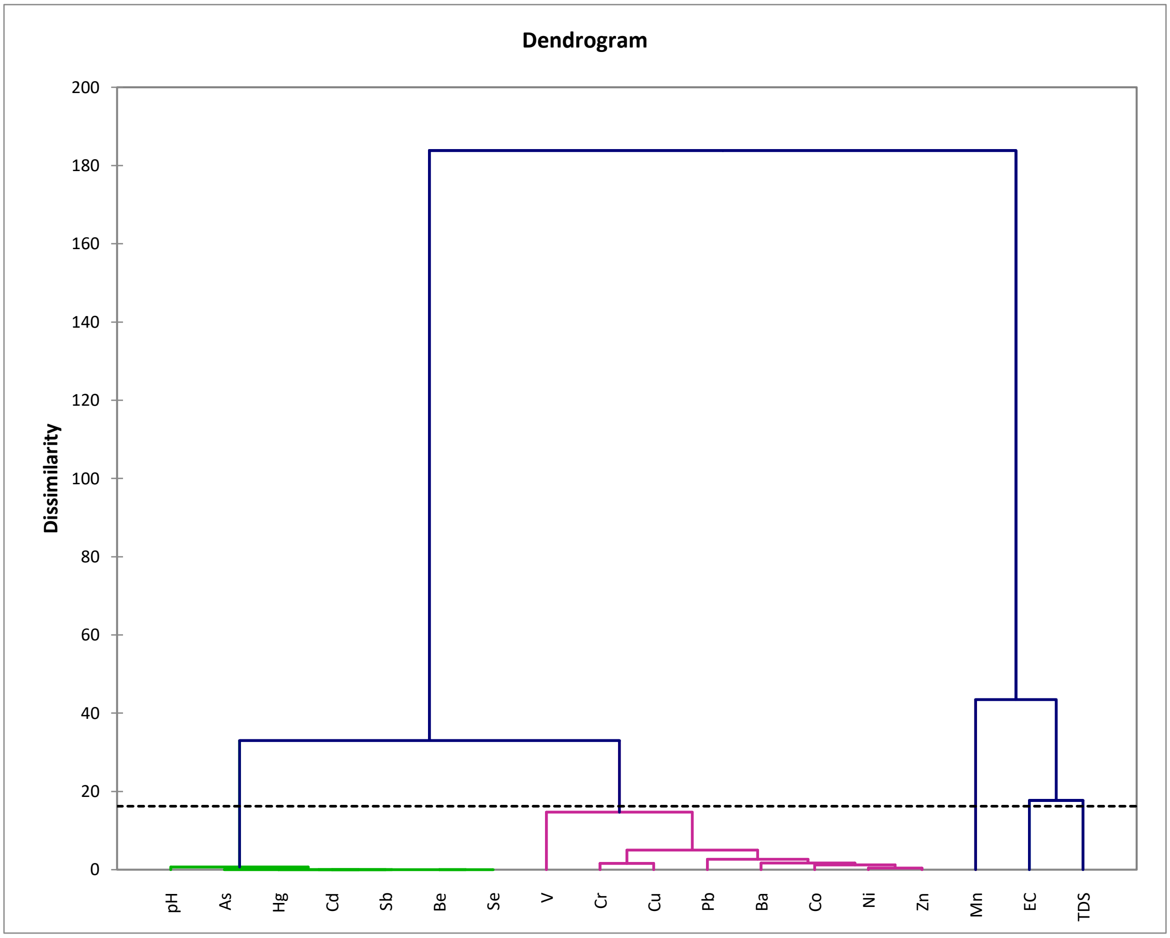


Figure 19: *Dendrogram showing the spatial clustering of trace metals in surrounding soil samples based on the hierarchical cluster analysis using Ward's method.*

Table 17: Pearson correlation matrix showing the relationship between the physicochemical parameters and trace metals in surrounding soils of geothermal springs

Variables	pH	EC	TDS	Be	V	Cr	Mn	Co	Ni	Cu	Zn	As	Se	Cd	Sb	Ba	Hg	Pb
pH	**1.00**																	
EC	-0.07	**1.00**																
TDS	-0.05	**0.86**	**1.00**															
Be	**-0.87**	0.07	0.03	**1.00**														
V	-0.34	-0.29	-0.32	**0.66**	**1.00**													
Cr	-0.27	-0.42	-0.37	**0.53**	**0.87**	**1.00**												
Mn	0.00	-0.23	-0.07	0.12	0.26	**0.67**	**1.00**											
Co	-0.35	-0.37	-0.40	**0.60**	**0.92**	**0.80**	0.23	**1.00**										
Ni	-0.22	-0.35	-0.29	**0.47**	**0.75**	**0.97**	**0.81**	**0.66**	**1.00**									
Cu	-0.32	-0.24	-0.27	**0.65**	**0.99**	**0.88**	0.32	**0.87**	**0.78**	**1.00**								
Zn	-0.23	-0.22	-0.22	**0.62**	**0.90**	**0.87**	0.42	**0.79**	**0.83**	**0.90**	**1.00**							
As	**-0.81**	0.46	0.38	**0.62**	-0.07	-0.19	-0.21	-0.11	-0.18	-0.04	-0.16	**1.00**						
Se	-0.29	-0.15	-0.16	**0.48**	0.29	0.20	-0.15	0.32	0.14	0.22	**0.49**	0.00	**1.00**					
Cd	-0.28	-0.20	-0.23	**0.62**	**0.95**	**0.86**	0.32	**0.79**	**0.78**	**0.98**	**0.89**	-0.04	0.20	**1.00**				
Sb	**-0.78**	**0.48**	0.41	**0.58**	-0.12	-0.23	-0.21	-0.17	-0.22	-0.09	-0.21	**1.00**	-0.04	-0.09	**1.00**			
Ba	**-0.87**	0.42	0.34	**0.72**	0.08	-0.07	-0.19	0.06	-0.09	0.10	-0.04	**0.98**	0.04	0.09	**0.97**	**1.00**		
Hg	0.15	0.06	0.06	-0.28	-0.33	0.04	0.45	-0.36	0.17	-0.28	-0.14	-0.15	-0.15	-0.22	-0.10	-0.21	**1.00**	
Pb	-0.18	-0.13	-0.16	**0.50**	**0.82**	**0.72**	0.29	**0.69**	**0.64**	**0.85**	**0.77**	-0.03	0.10	**0.78**	-0.06	0.08	-0.21	**1.00**

Values in bold are different from 0 with a significance level alpha=0.05

Table 18: Factor loadings of the trace metals concentrations and some physicochemical parameters of surrounding soils

	F1	F2	F3
pH	-0.377	-0.819	0.006
EC	-0.357	**0.536**	0.310
TDS	-0.355	0.463	0.404
Be	0.687	**0.693**	-0.046
V	**0.968**	0.023	-0.137
Cr	**0.946**	-0.168	0.237
Mn	**0.447**	-0.286	**0.746**
Co	**0.895**	-0.014	-0.240
Ni	**0.868**	-0.187	0.419
Cu	**0.966**	0.037	-0.043
Zn	**0.937**	-0.068	0.021
As	-0.063	**0.973**	**0.086**
Se	0.338	0.113	-0.423
Cd	**0.930**	0.027	0.013
Sb	-0.113	**0.963**	0.119
Ba	0.078	**0.978**	0.045
Hg	-0.200	-0.243	**0.731**
Pb	**0.811**	0.023	0.034
Eigenvalue	**7.963**	**4.709**	**1.867**
Variability (%)	**44.241**	**26.162**	**10.372**
Cumulative %	**44.241**	**70.403**	**80.776**

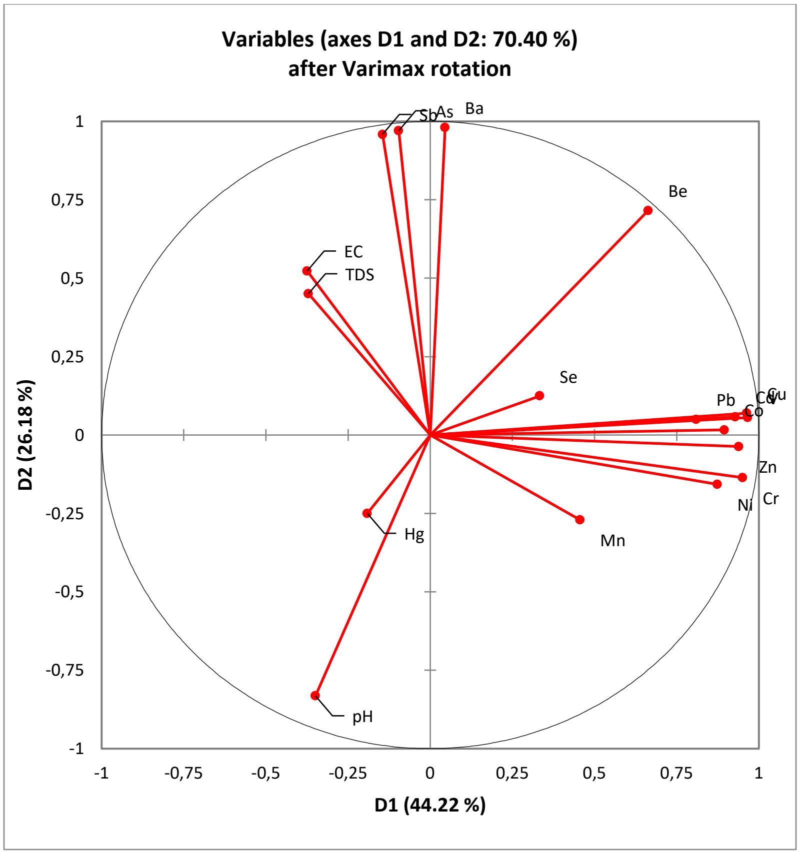


***Figure 20**: The principal component analysis (PCA) biplots showing the relationships between trace metals in the surrounding soils within the Soutpansberg region.*

4.5.1 Evaluation of human health risk due to trace metals from the surrounding soils

Trace metals concentrations in the topmost soil (0-10 cm) were considered in the risk assessment for both children and adults because of its closeness to the human activities such as agriculture and exposure to dust compared to deeper soils. The trace metals concentrations were used to estimate intake from different pathways (ingestion, inhalation and dermal) using standard USEPA's exposure equations highlighted above. Appendix 3 shows that the ingestion pathway is the major exposure to the surrounding soil at all sites followed by dermal and inhalation pathways. Hence, soil ingestion was the most significant contributor to the total health risk, except for a few trace metals that do not have RFD value for dermal exposure. Findings from this study also support the general observation that children are more susceptible/vulnerable to potential health risk associated with these trace metals in the environment (Figure 21) (USEPA, 1989; Makunda *et al.,* 2016; Hu *et al.,* 2017). The results from the ingestion, inhalation and dermal pathways for non-carcinogenic risks were presented in terms of HQs in Table 19.

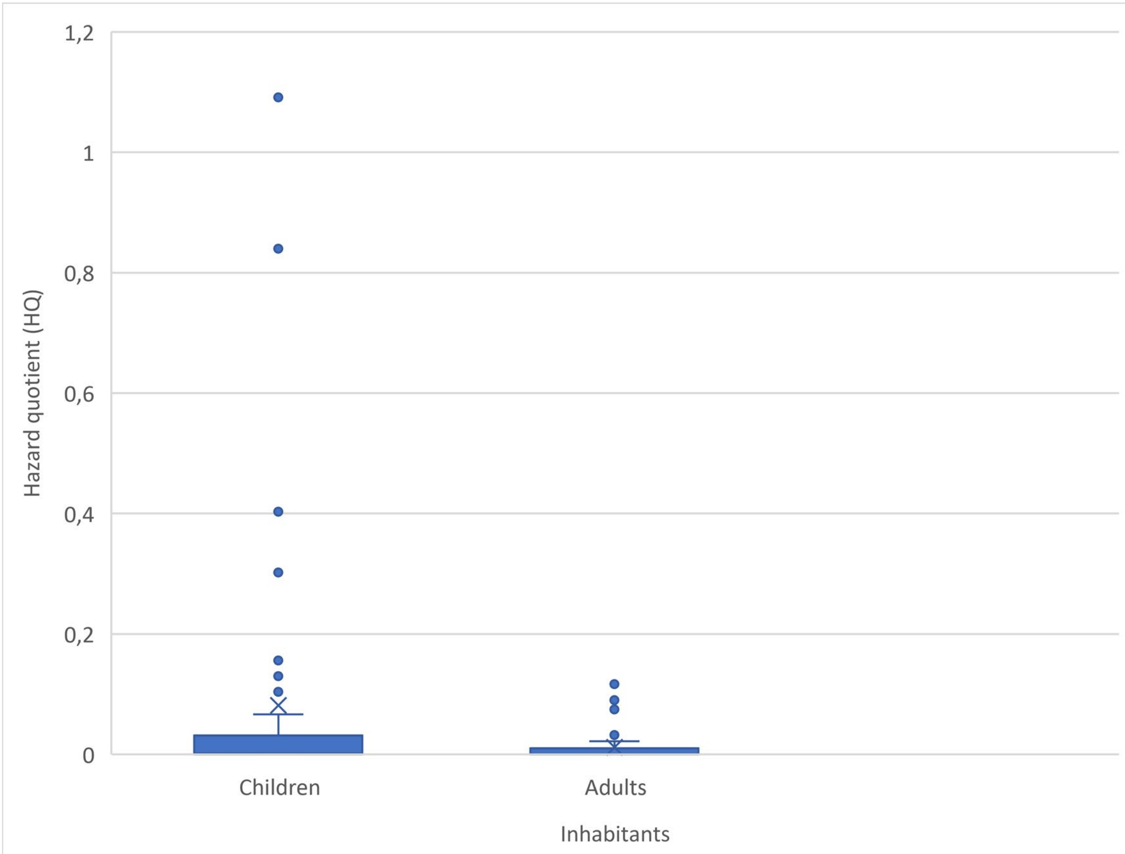


Figure 21: *Biplot variant of the hazard quotient risk among children and adults within Soutpansberg*

Table 19: Average daily intake (ADI) values in mg/kg/day for adults and children in surrounding soils from the geothermal springs for non-carcinogenic risk calculations within Soutpansberg region

	Be						V						Cr					
	Ingestion		inhalation		dermal		Ingestion		inhalation		dermal		Ingestion		inhalation		dermal	
	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults
TSS	2.40E-06	2.58E-07	6.60E-11	2.83E-11	5.05E-09	1.05E-08	2.19E-04	2.35E-05	6.02E-09	2.58E-09	4.60E-07	9.53E-07	5.91E-04	6.33E-05	1.62E-08	6.96E-09	1.24E-06	2.57E-06
TSW	2.89E-06	3.10E-07	7.94E-11	3.40E-11	6.07E-09	1.26E-08	2.34E-04	2.50E-05	6.42E-09	2.75E-09	4.91E-07	1.02E-06	4.79E-04	5.14E-05	1.32E-08	5.65E-09	1.01E-06	2.09E-06
SGS	1.41E-06	1.51E-07	3.86E-11	1.66E-11	2.95E-09	6.12E-09	8.78E-05	9.40E-06	2.41E-09	1.03E-09	1.84E-07	3.82E-07	1.28E-04	1.37E-05	3.50E-09	1.50E-09	2.68E-07	5.55E-07
SGW	1.19E-06	1.27E-07	3.27E-11	1.40E-11	2.50E-09	5.17E-09	8.35E-05	8.95E-06	2.30E-09	9.84E-10	1.75E-07	3.63E-07	9.99E-05	1.07E-05	2.74E-09	1.18E-09	2.10E-07	4.34E-07
SAW	7.52E-06	8.05E-07	2.07E-10	8.85E-11	1.58E-08	3.27E-08	2.11E-03	2.26E-04	5.80E-08	2.49E-08	4.43E-06	9.18E-06	1.16E-03	1.24E-04	3.18E-08	1.36E-08	2.43E-06	5.04E-06
MPS	8.00E-06	8.58E-07	2.20E-10	9.42E-11	1.68E-08	3.48E-08	8.72E-04	9.34E-05	2.39E-08	1.03E-08	1.83E-06	3.79E-06	4.62E-04	4.95E-05	1.27E-08	5.43E-09	9.69E-07	2.01E-06
MPW	2.53E-06	2.71E-07	6.95E-11	2.98E-11	5.32E-09	1.10E-08	6.27E-04	6.72E-05	1.72E-08	7.38E-09	1.32E-06	2.73E-06	3.57E-04	3.82E-05	9.81E-09	4.20E-09	7.50E-07	1.55E-06
	Mn						Co						Ni					
TSS	1.45E-03	1.55E-04	3.98E-08	1.70E-08	3.04E-06	6.30E-06	6.50E-05	6.96E-06	1.79E-09	7.65E-10	1.37E-07	2.83E-07	4.40E-04	4.72E-05	1.21E-08	5.18E-09	9.25E-07	1.92E-06
TSW	1.67E-03	1.78E-04	4.58E-08	1.96E-08	3.50E-06	7.25E-06	6.34E-05	6.79E-06	1.74E-09	7.47E-10	1.33E-07	2.76E-07	3.34E-04	3.58E-05	9.17E-09	3.93E-09	7.01E-07	1.45E-06
SGS	8.79E-04	9.42E-05	2.42E-08	1.04E-08	1.85E-06	3.82E-06	2.93E-05	3.14E-06	8.05E-10	3.45E-10	6.16E-08	1.28E-07	1.44E-04	1.54E-05	3.96E-09	1.70E-09	3.03E-07	6.27E-07
SGW	6.90E-04	7.39E-05	1.90E-08	8.12E-09	1.45E-06	3.00E-06	1.94E-05	2.08E-06	5.33E-10	2.29E-10	4.08E-08	8.44E-08	7.84E-05	8.40E-06	2.15E-09	9.23E-10	1.65E-07	3.41E-07
SAW	1.51E-03	1.62E-04	4.16E-08	1.78E-08	3.18E-06	6.58E-06	3.66E-04	3.93E-05	1.01E-08	4.31E-09	7.70E-07	1.59E-06	6.60E-04	7.08E-05	1.81E-08	7.78E-09	1.39E-06	2.87E-06
MPS	4.53E-04	4.85E-05	1.24E-08	5.33E-09	9.51E-07	1.97E-06	1.87E-04	2.01E-05	5.15E-09	2.21E-09	3.94E-07	8.15E-07	2.70E-04	2.89E-05	7.41E-09	3.18E-09	5.67E-07	1.17E-06
MPW	6.00E-04	6.43E-05	1.65E-08	7.07E-09	1.26E-06	2.61E-06	2.44E-04	2.62E-05	6.72E-09	2.88E-09	5.13E-07	1.06E-06	1.48E-04	1.59E-05	4.07E-09	1.75E-09	3.11E-07	6.45E-07
	Cu						Zn						As					
TSS	1.62E-04	1.74E-05	4.46E-09	1.91E-09	3.41E-07	7.06E-07	1.95E-04	2.09E-05	5.35E-09	2.29E-09	4.09E-07	8.48E-07	4.88E-06	5.23E-07	1.34E-10	5.75E-11	1.03E-08	2.12E-08
TSW	1.76E-04	1.88E-05	4.82E-09	2.07E-09	3.69E-07	7.64E-07	2.06E-04	2.21E-05	5.67E-09	2.43E-09	4.34E-07	8.98E-07	4.72E-06	5.05E-07	1.30E-10	5.55E-11	9.91E-09	2.05E-08
SGS	1.11E-04	1.19E-05	3.05E-09	1.31E-09	2.33E-07	4.83E-07	2.20E-04	2.35E-05	6.03E-09	2.58E-09	4.61E-07	9.55E-07	4.26E-06	4.56E-07	1.17E-10	5.01E-11	8.94E-09	1.85E-08
SGW	9.13E-05	9.78E-06	2.51E-09	1.07E-09	1.92E-07	3.97E-07	6.30E-05	6.75E-06	1.73E-09	7.42E-10	1.32E-07	2.74E-07	7.51E-06	8.04E-07	2.06E-10	8.84E-11	1.58E-08	3.26E-08
SAW	1.24E-03	1.33E-04	3.41E-08	1.46E-08	2.61E-06	5.40E-06	6.22E-04	6.66E-05	1.71E-08	7.32E-09	1.31E-06	2.70E-06	1.01E-05	1.08E-06	2.76E-10	1.18E-10	2.11E-08	4.38E-08
MPS	4.28E-04	4.58E-05	1.17E-08	5.04E-09	8.98E-07	1.86E-06	4.83E-04	5.17E-05	1.33E-08	5.68E-09	1.01E-06	2.10E-06	1.40E-05	1.50E-06	3.86E-10	1.65E-10	2.95E-08	6.11E-08
MPW	2.47E-04	2.64E-05	6.78E-09	2.91E-09	5.18E-07	1.07E-06	1.03E-04	1.11E-05	2.84E-09	1.22E-09	2.17E-07	4.49E-07	1.32E-06	1.41E-07	3.62E-11	1.55E-11	2.77E-09	5.73E-09

	Se						Cd						Sb					
	Ingestion		**inhalation**		**dermal**		**Ingestion**		**inhalation**		**dermal**		**Ingestion**		**inhalation**		**dermal**	
	Children	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**
TSS	3.45E-06	3.70E-07	9.48E-11	4.06E-11	7.25E-09	1.50E-08	4.35E-07	4.66E-08	1.19E-11	5.12E-12	9.13E-10	1.89E-09	1.79E-07	1.92E-08	4.92E-12	2.11E-12	3.76E-10	7.79E-10
TSW	2.26E-06	2.42E-07	6.22E-11	2.66E-11	4.75E-09	9.84E-09	3.07E-07	3.29E-08	8.43E-12	3.61E-12	6.44E-10	1.33E-09	2.68E-07	2.88E-08	7.38E-12	3.16E-12	5.64E-10	1.17E-09
SGS	8.95E-07	9.59E-08	2.46E-11	1.05E-11	1.88E-09	3.89E-09	2.81E-07	3.01E-08	7.73E-12	3.31E-12	5.91E-10	1.22E-09	2.43E-07	2.60E-08	6.67E-12	2.86E-12	5.10E-10	1.06E-09
SGW	1.25E-06	1.34E-07	3.44E-11	1.48E-11	2.63E-09	5.45E-09	1.28E-07	1.37E-08	3.51E-12	1.51E-12	2.68E-10	5.56E-10	2.56E-07	2.74E-08	7.02E-12	3.01E-12	5.37E-10	1.11E-09
SAW	3.38E-06	3.62E-07	9.27E-11	3.97E-11	7.09E-09	1.47E-08	3.29E-06	3.52E-07	9.03E-11	3.87E-11	6.90E-09	1.43E-08	3.71E-07	3.97E-08	1.02E-11	4.37E-12	7.79E-10	1.61E-09
MPS	1.96E-05	2.10E-06	5.39E-10	2.31E-10	4.12E-08	8.53E-08	1.20E-06	1.29E-07	3.30E-11	1.42E-11	2.52E-09	5.23E-09	4.73E-07	5.07E-08	1.30E-11	5.57E-12	9.93E-10	2.06E-09
MPW	1.46E-06	1.56E-07	4.00E-11	1.72E-11	3.06E-09	6.34E-09	2.30E-07	2.47E-08	6.32E-12	2.71E-12	4.83E-10	1.00E-09	1.28E-07	1.37E-08	3.51E-12	1.51E-12	2.68E-10	5.56E-10
	Ba						**Hg**						**Pb**					
TSS	1.57E-04	1.68E-05	4.32E-09	1.85E-09	3.30E-07	6.84E-07	2.93E-06	3.14E-07	8.04E-11	3.45E-11	6.15E-09	1.27E-08	3.01E-05	3.23E-06	8.28E-10	3.55E-10	6.33E-08	1.31E-07
TSW	1.86E-04	1.99E-05	5.10E-09	2.18E-09	3.90E-07	8.07E-07	8.44E-07	9.04E-08	2.32E-11	9.94E-12	1.77E-09	3.67E-09	3.78E-05	4.05E-06	1.04E-09	4.45E-10	7.94E-08	1.65E-07
SGS	1.35E-04	1.44E-05	3.70E-09	1.59E-09	2.83E-07	5.86E-07	1.51E-06	1.62E-07	4.14E-11	1.78E-11	3.17E-09	6.56E-09	7.78E-05	8.33E-06	2.14E-09	9.16E-10	1.63E-07	3.38E-07
SGW	2.54E-04	2.72E-05	6.98E-09	2.99E-09	5.33E-07	1.11E-06	1.28E-08	1.37E-09	3.51E-13	1.51E-13	2.68E-11	5.56E-11	1.90E-05	2.04E-06	5.22E-10	2.24E-10	3.99E-08	8.26E-08
SAW	6.19E-04	6.63E-05	1.70E-08	7.29E-09	1.30E-06	2.69E-06	1.28E-08	1.37E-09	3.51E-13	1.51E-13	2.68E-11	5.56E-11	1.09E-03	1.16E-04	2.99E-08	1.28E-08	2.28E-06	4.73E-06
MPS	5.80E-04	6.21E-05	1.59E-08	6.83E-09	1.22E-06	2.52E-06	6.39E-08	6.85E-09	1.76E-12	7.53E-13	1.34E-10	2.78E-10	1.21E-04	1.29E-05	3.32E-09	1.42E-09	2.54E-07	5.26E-07
MPW	2.31E-04	2.47E-05	6.33E-09	2.71E-09	4.84E-07	1.00E-06	1.28E-08	1.37E-09	3.51E-13	1.51E-13	2.68E-11	5.56E-11	3.79E-05	4.06E-06	1.04E-09	4.46E-10	7.96E-08	1.65E-07

When HQ and HI values are less than a unit, there is no obvious risk to the population, but if these values exceed one, there may be concern for potential non-carcinogenic effects (USEPA, 2004) as explained earlier. Most of these metals are associated with negative neurological impacts on humans (e.g. mental retardation and developmental delay) (Jacob *et al.,* 2002; Madl *et al.,* 2007; Bouchard *et al.,* 2008). For both children and adults, the calculated HQ was less than one for the three pathways within Soutpansberg. This implies that there is no significant non-carcinogenic risk in their population. The total HQ for Cr in child population was, however, greater than one and therefore implies that there is a possible non-carcinogenic risk to their population. Hence, there is a need for necessary mitigation strategies to reduce concentrations and limit human exposure in the selected communities. Also, the HI values were less than one in both populations at all sites implying that there is no significant non-carcinogenic risk to their population, but the relatively high value of Cr is of great concern as explained (Table 20)

The excess lifetime cancer risks for adults and children are calculated separately from the average concentrations of individual metals in soil for all the exposure pathways using equations (7-9). Based on the carcinogenic risk values of the calculated ADI and HQ values presented in Tables 21 and 22, respectively, the results of the excess lifetime cancer risk are presented in Table 23. The HQ values for the three exposure pathways were presented in Appendix 4.

Table 20: Hazard index (HI) for non-carcinogenic risk for the surrounding soils within Soutpansberg region.

		TSS	TSW	SGS	SGW	SAW	MPS	MPW
Be	Children	1.20E-02	1.44E-02	7.03E-03	5.95E-03	3.76E-02	4.00E-02	1.27E-02
	Adults	1.29E-03	1.55E-03	7.54E-04	6.37E-04	4.03E-03	4.29E-03	1.36E-03
V	Children	4.35E-02	4.63E-02	1.74E-02	1.66E-02	4.19E-01	1.73E-01	1.24E-01
	Adults	4.66E-03	4.97E-03	1.87E-03	1.78E-03	4.49E-02	1.85E-02	1.33E-02
Cr	Children	1.98E-01	1.61E-01	4.27E-02	3.34E-02	3.88E-01	1.55E-01	1.20E-01
	Adults	2.22E-02	1.80E-02	4.79E-03	3.75E-03	4.35E-02	1.73E-02	1.34E-02
Mn	Children	6.24E-02	7.19E-02	3.79E-02	2.98E-02	6.52E-02	1.95E-02	2.59E-02
	Adults	1.09E-02	1.25E-02	6.60E-03	5.18E-03	1.14E-02	3.40E-03	4.51E-03
Co	Children	5.68E-03	5.54E-03	2.56E-03	1.69E-03	3.20E-02	1.64E-02	2.13E-02
	Adults	5.32E-03	5.19E-03	2.40E-03	1.59E-03	3.00E-02	1.53E-02	2.00E-02
Ni	Children	2.22E-02	1.68E-02	7.26E-03	3.95E-03	3.33E-02	1.36E-02	7.47E-03
	Adults	2.70E-03	2.05E-03	8.84E-04	4.81E-04	4.05E-03	1.65E-03	9.10E-04
Cu	Children	4.40E-03	4.76E-03	3.01E-03	2.48E-03	3.37E-02	1.16E-02	6.69E-03
	Adults	5.00E-04	5.40E-04	3.42E-04	2.81E-04	3.82E-03	1.32E-03	7.59E-04
Zn	Children	6.55E-04	6.94E-04	7.38E-04	2.12E-04	2.09E-03	1.62E-03	3.47E-04
	Adults	8.09E-05	8.57E-05	9.11E-05	2.62E-05	2.58E-04	2.00E-04	4.29E-05
As	Children	1.63E-02	1.58E-02	1.42E-02	2.51E-02	3.36E-02	4.69E-02	4.40E-03
	Adults	1.82E-03	1.75E-03	1.58E-03	2.79E-03	3.74E-03	5.22E-03	4.89E-04
Se	Children	6.90E-04	4.53E-04	1.79E-04	2.51E-04	6.75E-04	3.92E-03	2.92E-04
	Adults	7.40E-05	4.85E-05	1.92E-05	2.69E-05	7.23E-05	4.20E-04	3.12E-05
Cd	Children	4.36E-04	3.08E-04	2.82E-04	1.28E-04	3.29E-03	1.20E-03	2.31E-04
	Adults	4.86E-05	3.43E-05	3.14E-05	1.43E-05	3.67E-04	1.34E-04	2.57E-05
Sb	Children	4.48E-04	6.71E-04	6.07E-04	6.39E-04	9.27E-04	1.18E-03	3.20E-04
	Adults	4.80E-05	7.19E-05	6.51E-05	6.85E-05	9.93E-05	1.27E-04	3.43E-05
Ba	Children	7.86E-04	9.28E-04	6.74E-04	1.27E-03	3.09E-03	2.90E-03	1.15E-03
	Adults	8.42E-05	9.94E-05	7.22E-05	1.36E-04	3.32E-04	3.11E-04	1.24E-04
Hg	Children	9.78E-03	2.82E-03	5.04E-03	4.27E-05	4.27E-05	2.14E-04	4.27E-05
	Adults	1.09E-03	3.14E-04	5.61E-04	4.75E-06	4.75E-06	2.38E-05	4.75E-06
Pb	Children	8.73E-03	1.10E-02	2.25E-02	5.50E-03	3.15E-01	3.50E-02	1.10E-02
	Adults	1.17E-03	1.47E-03	3.03E-03	7.39E-04	4.23E-02	4.70E-03	1.47E-03

Table 21: Average daily intake (ADI) values in mg/kg/day for adults and children in surrounding soils from the geothermal springs for carcinogenic risk calculations within Soutpansberg region.

	Be						V						Cr					
	Ingestion		Inhalation		dermal		Ingestion		inhalation		dermal		Ingestion		inhalation		dermal	
	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults
TSS	2.06E-07	1.10E-07	5.66E-12	1.21E-11	4.33E-10	4.48E-09	1.88E-05	1.01E-06	5.16E-10	1.11E-10	3.94E-08	4.08E-07	5.07E-05	2.71E-05	1.39E-09	2.98E-10	1.06E-07	1.10E-06
TSW	2.48E-07	1.33E-07	6.80E-12	1.46E-11	6.07E-09	5.39E-09	2.00E-05	1.07E-06	5.50E-10	1.18E-10	4.20E-08	4.35E-07	4.11E-05	2.20E-05	1.13E-09	2.42E-10	8.63E-08	8.94E-07
SGS	1.21E-07	6.46E-08	3.31E-12	7.10E-12	2.95E-09	2.62E-09	7.52E-06	4.03E-07	2.07E-10	4.43E-11	1.58E-08	1.64E-07	1.09E-05	5.86E-06	3.00E-10	6.44E-11	2.30E-08	2.38E-07
SGW	1.02E-07	5.46E-08	2.80E-12	6.00E-12	2.50E-09	2.22E-09	7.16E-06	3.84E-07	1.97E-10	4.22E-11	1.50E-08	1.56E-07	8.56E-06	4.59E-06	2.35E-10	5.04E-11	1.80E-08	1.86E-07
SAW	6.44E-07	3.45E-07	1.77E-11	3.79E-11	1.58E-08	1.40E-08	1.81E-04	9.69E-06	4.97E-09	1.07E-09	3.80E-07	3.94E-06	9.92E-05	5.32E-05	2.73E-09	5.84E-10	2.08E-07	2.16E-06
MPS	6.86E-07	3.68E-07	1.88E-11	4.04E-11	1.68E-08	1.49E-08	7.47E-05	4.00E-06	2.05E-09	4.40E-10	1.57E-07	1.62E-06	3.96E-05	2.12E-05	1.09E-09	2.33E-10	8.31E-08	8.60E-07
MPW	2.17E-07	1.16E-07	5.96E-12	1.28E-11	5.32E-09	4.72E-09	5.37E-05	2.88E-06	1.48E-09	3.16E-10	1.13E-07	1.17E-06	3.06E-05	1.64E-05	8.41E-10	1.80E-10	6.43E-08	6.65E-07
	Mn						Co						Ni					
TSS	1.24E-04	6.65E-05	3.41E-09	7.30E-09	2.61E-07	2.70E-06	5.57E-06	2.98E-06	1.53E-10	3.28E-10	1.17E-08	1.21E-07	3.77E-05	2.02E-05	1.04E-09	2.22E-09	7.93E-08	8.21E-07
TSW	1.43E-04	7.65E-05	3.92E-09	8.41E-09	3.00E-07	3.11E-06	5.44E-06	2.91E-06	1.49E-10	3.20E-10	1.14E-08	1.18E-07	2.86E-05	1.53E-05	7.86E-10	1.68E-09	6.01E-08	6.22E-07
SGS	7.54E-05	4.04E-05	2.07E-09	4.44E-09	1.58E-07	1.64E-06	2.51E-06	1.35E-06	6.90E-11	1.48E-10	5.28E-09	5.47E-08	1.24E-05	6.62E-06	3.39E-10	7.27E-10	2.59E-08	2.69E-07
SGW	5.91E-05	3.17E-05	1.62E-09	3.48E-09	1.24E-07	1.29E-06	1.66E-06	8.91E-07	4.57E-11	9.79E-11	3.49E-09	3.62E-08	6.72E-06	3.60E-06	1.85E-10	3.95E-10	1.41E-08	1.46E-07
SAW	1.30E-04	6.95E-05	3.56E-09	7.63E-09	2.72E-07	2.82E-06	3.14E-05	1.68E-05	8.63E-10	1.85E-09	6.60E-08	6.83E-07	5.66E-05	3.03E-05	1.56E-09	3.33E-09	1.19E-07	1.23E-06
MPS	3.88E-05	2.08E-05	1.07E-09	2.28E-09	8.15E-08	8.44E-07	1.61E-05	8.61E-06	4.41E-10	9.46E-10	3.37E-08	3.49E-07	2.31E-05	1.24E-05	6.35E-10	1.36E-09	4.86E-08	5.03E-07
MPW	5.15E-05	2.76E-05	1.41E-09	3.03E-09	1.08E-07	1.12E-06	2.10E-05	1.12E-05	5.76E-10	1.23E-09	4.40E-08	4.56E-07	1.27E-05	6.81E-06	3.49E-10	7.48E-10	2.67E-08	2.76E-07
	Cu						Zn						As					
TSS	1.39E-05	7.46E-06	3.82E-10	8.19E-10	2.92E-08	3.03E-07	1.67E-05	8.95E-06	4.59E-10	9.83E-10	3.51E-08	3.63E-07	4.19E-07	2.24E-07	1.15E-11	2.46E-11	8.79E-10	9.11E-09
TSW	1.50E-05	8.06E-06	4.13E-10	8.86E-10	3.16E-08	3.27E-07	1.77E-05	9.48E-06	4.86E-10	1.04E-09	3.72E-08	3.85E-07	4.04E-07	2.17E-07	1.11E-11	2.38E-11	8.49E-10	8.80E-09
SGS	9.52E-06	5.10E-06	2.62E-10	5.60E-10	2.00E-08	2.07E-07	1.88E-05	1.01E-05	5.17E-10	1.11E-09	3.95E-08	4.09E-07	3.65E-07	1.95E-07	1.00E-11	2.15E-11	7.66E-10	7.94E-09
SGW	7.83E-06	4.19E-06	2.15E-10	4.61E-10	1.64E-08	1.70E-07	5.40E-06	2.89E-06	1.48E-10	3.18E-10	1.13E-08	1.18E-07	6.43E-07	3.45E-07	1.77E-11	3.79E-11	1.35E-09	1.40E-08
SAW	1.06E-04	5.70E-05	2.92E-09	6.26E-09	2.23E-07	2.31E-06	5.33E-05	2.85E-05	1.46E-09	3.14E-09	1.12E-07	1.16E-06	8.62E-07	4.62E-07	2.37E-11	5.08E-11	1.81E-09	1.88E-08
MPS	3.67E-05	1.96E-05	1.01E-09	2.16E-09	7.70E-08	7.97E-07	4.14E-05	2.22E-05	1.14E-09	2.43E-09	8.69E-08	9.00E-07	1.20E-06	6.45E-07	3.31E-11	7.08E-11	2.53E-09	2.62E-08
MPW	2.12E-05	1.13E-05	5.81E-10	1.25E-09	4.44E-08	4.60E-07	8.86E-06	4.74E-06	2.43E-10	5.21E-10	1.86E-08	1.93E-07	1.13E-07	6.05E-08	3.10E-12	6.65E-12	2.37E-10	2.46E-09

	Se						Cd						Sb					
	Ingestion		Inhalation		dermal		Ingestion		inhalation		dermal		Ingestion		inhalation		dermal	
	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults
TSS	2.96E-07	1.59E-07	8.13E-12	1.74E-11	6.21E-10	6.44E-09	3.73E-08	2.00E-08	1.02E-12	2.19E-12	7.82E-11	8.10E-10	1.53E-08	8.22E-09	4.21E-13	9.03E-13	3.22E-11	3.34E-10
TSW	1.94E-07	1.04E-07	5.33E-12	1.14E-11	4.07E-10	4.22E-09	2.63E-08	1.41E-08	7.23E-13	1.55E-12	5.52E-11	5.72E-10	2.30E-08	1.23E-08	6.32E-13	1.35E-12	4.83E-11	5.01E-10
SGS	7.67E-08	4.11E-08	2.11E-12	4.52E-12	1.61E-10	1.67E-09	2.41E-08	1.29E-08	6.62E-13	1.42E-12	5.06E-11	5.24E-10	2.08E-08	1.12E-08	5.72E-13	1.23E-12	4.37E-11	4.53E-10
SGW	1.07E-07	5.75E-08	2.95E-12	6.32E-12	2.26E-10	2.34E-09	1.10E-08	5.87E-09	3.01E-13	6.45E-13	2.30E-11	2.38E-10	2.19E-08	1.17E-08	6.02E-13	1.29E-12	4.60E-11	4.77E-10
SAW	2.89E-07	1.55E-07	7.95E-12	1.70E-11	6.08E-10	6.29E-09	2.82E-07	1.51E-07	7.74E-12	1.66E-11	5.91E-10	6.13E-09	3.18E-08	1.70E-08	8.73E-13	1.87E-12	6.67E-11	6.91E-10
MPS	1.68E-06	9.01E-07	4.62E-11	9.90E-11	3.53E-09	3.66E-08	1.03E-07	5.52E-08	2.83E-12	6.06E-12	2.16E-10	2.24E-09	4.05E-08	2.17E-08	1.11E-12	2.39E-12	8.52E-11	8.82E-10
MPW	1.25E-07	6.69E-08	3.43E-12	7.35E-12	2.62E-10	2.72E-09	1.97E-08	1.06E-08	5.42E-13	1.16E-12	4.14E-11	4.29E-10	1.10E-08	5.87E-09	3.01E-13	6.45E-13	2.30E-11	2.38E-10
	Ba						Hg						Pb					
TSS	1.35E-05	7.22E-06	3.70E-10	7.93E-10	2.83E-08	2.93E-07	2.51E-07	1.34E-07	6.89E-12	1.48E-11	5.27E-10	5.46E-09	2.58E-06	1.38E-07	7.10E-11	1.52E-10	5.43E-09	5.62E-08
TSW	1.59E-05	8.52E-06	4.37E-10	9.36E-10	3.34E-08	3.46E-07	7.23E-08	3.87E-08	1.99E-12	4.26E-12	1.52E-10	1.57E-09	3.24E-06	1.74E-07	8.91E-11	1.91E-10	6.81E-09	7.05E-08
SGS	1.16E-05	6.19E-06	3.17E-10	6.80E-10	2.43E-08	2.51E-07	1.29E-07	6.93E-08	3.55E-12	7.61E-12	2.72E-10	2.81E-09	6.67E-06	3.57E-07	1.83E-10	3.93E-10	1.40E-08	1.45E-07
SGW	2.18E-05	1.17E-05	5.98E-10	1.28E-09	4.57E-08	4.74E-07	1.10E-09	5.87E-10	3.01E-14	6.45E-14	2.30E-12	2.38E-11	1.63E-06	8.72E-08	4.47E-11	9.59E-11	3.42E-09	3.54E-08
SAW	5.30E-05	2.84E-05	1.46E-09	3.12E-09	1.11E-07	1.15E-06	1.10E-09	5.87E-10	3.01E-14	6.45E-14	2.30E-12	2.38E-11	9.32E-05	4.99E-06	2.56E-09	5.49E-09	1.96E-07	2.03E-06
MPS	4.97E-05	2.66E-05	1.37E-09	2.93E-09	1.04E-07	1.08E-06	5.48E-09	2.94E-09	1.51E-13	3.23E-13	1.15E-11	1.19E-10	1.04E-05	5.55E-07	2.85E-10	6.10E-10	2.18E-08	2.25E-07
MPW	1.98E-05	1.06E-05	5.43E-10	1.16E-09	4.15E-08	4.30E-07	1.10E-09	5.87E-10	3.01E-14	6.45E-14	2.30E-12	2.38E-11	3.25E-06	1.74E-07	8.92E-11	1.91E-10	6.82E-09	7.06E-08

Table 22: Hazard index for carcinogenic risk for the surrounding soils within Soutpansberg region.

		TSS	TSW	SGS	SGW	SAW	MPS	MPW
Be	Children	1.03E-03	1.24E-03	6.03E-04	5.10E-04	3.22E-03	3.43E-03	1.08E-03
	Adults	5.52E-04	6.63E-04	3.23E-04	2.73E-04	1.73E-03	1.84E-03	5.81E-04
V	Children	3.72E-03	3.97E-03	1.49E-03	1.42E-03	3.59E-02	1.48E-02	1.07E-02
	Adults	2.00E-04	2.13E-04	8.00E-05	7.61E-05	1.92E-03	7.94E-04	5.71E-04
Cr	Children	1.70E-02	1.38E-02	3.66E-03	2.87E-03	3.32E-02	1.33E-02	1.02E-02
	Adults	9.42E-03	7.64E-03	2.03E-03	1.59E-03	1.85E-02	7.36E-03	5.69E-03
Mn	Children	5.35E-03	6.16E-03	3.25E-03	2.55E-03	5.59E-03	1.67E-03	2.22E-03
	Adults	4.66E-03	5.36E-03	2.83E-03	2.22E-03	4.87E-03	1.46E-03	1.93E-03
Co	Children	4.87E-04	4.75E-04	2.19E-04	1.45E-04	2.74E-03	1.40E-03	1.83E-03
	Adults	2.28E-03	2.23E-03	1.03E-03	6.81E-04	1.29E-02	6.58E-03	8.58E-03
Ni	Children	1.90E-03	1.44E-03	6.22E-04	3.38E-04	2.85E-03	1.16E-03	6.40E-04
	Adults	1.16E-03	8.77E-04	3.79E-04	2.06E-04	1.74E-03	7.09E-04	3.90E-04
Cu	Children	3.77E-04	4.08E-04	2.58E-04	2.12E-04	2.88E-03	9.94E-04	5.74E-04
	Adults	2.14E-04	2.32E-04	1.46E-04	1.20E-04	1.64E-03	5.64E-04	3.25E-04
Zn	Children	5.61E-05	5.95E-05	6.33E-05	1.82E-05	1.79E-04	1.39E-04	2.98E-05
	Adults	3.47E-05	3.67E-05	3.91E-05	1.12E-05	1.11E-04	8.59E-05	1.84E-05
As	Children	1.40E-03	1.35E-03	1.22E-03	2.15E-03	2.88E-03	4.02E-03	3.77E-04
	Adults	7.78E-04	7.52E-04	6.78E-04	1.20E-03	1.60E-03	2.24E-03	2.10E-04
Se	Children	5.92E-05	3.88E-05	1.53E-05	2.15E-05	5.79E-05	3.36E-04	2.50E-05
	Adults	3.17E-05	2.08E-05	8.22E-06	1.15E-05	3.10E-05	1.80E-04	1.34E-05
Cd	Children	3.74E-05	2.64E-05	2.42E-05	1.10E-05	2.82E-04	1.03E-04	1.98E-05
	Adults	2.08E-05	1.47E-05	1.35E-05	6.12E-06	1.57E-04	5.75E-05	1.10E-05
Sb	Children	3.84E-05	5.75E-05	5.21E-05	5.48E-05	7.95E-05	1.01E-04	2.74E-05
	Adults	2.06E-05	3.08E-05	2.79E-05	2.94E-05	4.26E-05	5.43E-05	1.47E-05
Ba	Children	6.73E-05	7.95E-05	5.78E-05	1.09E-04	2.65E-04	2.49E-04	9.88E-05
	Adults	3.61E-05	4.26E-05	3.09E-05	5.83E-05	1.42E-04	1.33E-04	5.29E-05
Hg	Children	8.38E-04	2.42E-04	4.32E-04	3.66E-06	3.66E-06	1.83E-05	3.66E-06
	Adults	4.67E-04	1.34E-04	2.40E-04	2.04E-06	2.04E-06	1.02E-05	2.04E-06
Pb	Children	7.49E-04	9.39E-04	1.93E-03	4.72E-04	2.70E-02	3.00E-03	9.41E-04
	Adults	1.47E-04	1.84E-04	3.78E-04	9.24E-05	5.29E-03	5.88E-04	1.84E-04

The carcinogenic risk was calculated for trace metals (As, Cd, Cr, Co and Pb) with an available carcinogenic slope factor from literature (Table 6). Cr, As and Co were found to be the highest contributors (value greater than recommended standard from 10^{-4} to 10^{-6}) to cancer risk in the selected communities. Cd does not pose cancer risk to children at all the sites except for Siloam (SAW). The cancer risk from winter to summer ranges from 1.56E-02 to 1.37E-02; 2.84E-02 to 2.69E-02; 5.98E-03 to 6.15E-02; 1.22E-02 to 9.30E-03; 2.71E-02 to 2.38E-02; 7.19E-02 to 8.73E-02 for children and adults, respectively (Figure 22). There is high possibility of cancer risk at the study areas and there is need for intervention. Therefore, the cancer risk is high in the general population, that is 1 in 72-162 individuals in children's population and 1 in 7-107 individuals for adult population. The ingestion route seems to be the major contributor to excess lifetime cancer risk followed by the dermal pathway. This quantitative evidence demonstrates the critical need for clinical study and then mitigation strategies to protect the residents especially the children.

Table 23: Carcinogenic risk assessment of Cr, Cd, As, Co and Pb from surrounding soils within Soutpansberg region.

	Cr		Cd		As		Pb		Co	
	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults
TSS	8.48E-03	4.71E-03	2.35E-04	1.31E-04	2.10E-03	1.17E-03	6.36E-06	1.25E-06	4.77E-03	2.24E-02
TSW	6.88E-03	3.82E-03	1.66E-04	9.25E-05	2.03E-03	1.13E-03	7.99E-06	1.56E-06	4.65E-03	2.18E-02
SGS	1.83E-03	1.02E-03	1.52E-04	8.48E-05	1.83E-03	1.02E-03	1.64E-05	3.22E-06	2.15E-03	1.01E-02
SGW	1.43E-03	7.96E-04	6.92E-05	3.86E-05	3.22E-03	1.79E-03	4.01E-06	7.86E-07	1.42E-03	6.67E-03
SAW	1.66E-02	9.23E-03	1.78E-03	9.91E-04	4.32E-03	2.40E-03	2.29E-04	4.49E-05	2.69E-02	1.26E-01
MPS	6.63E-03	3.68E-03	6.51E-04	3.62E-04	6.03E-03	3.35E-03	2.55E-05	5.00E-06	1.37E-02	6.45E-02
MPW	5.12E-03	2.85E-03	1.25E-04	6.94E-05	5.66E-04	3.15E-04	8.00E-06	1.57E-06	1.79E-02	8.41E-02

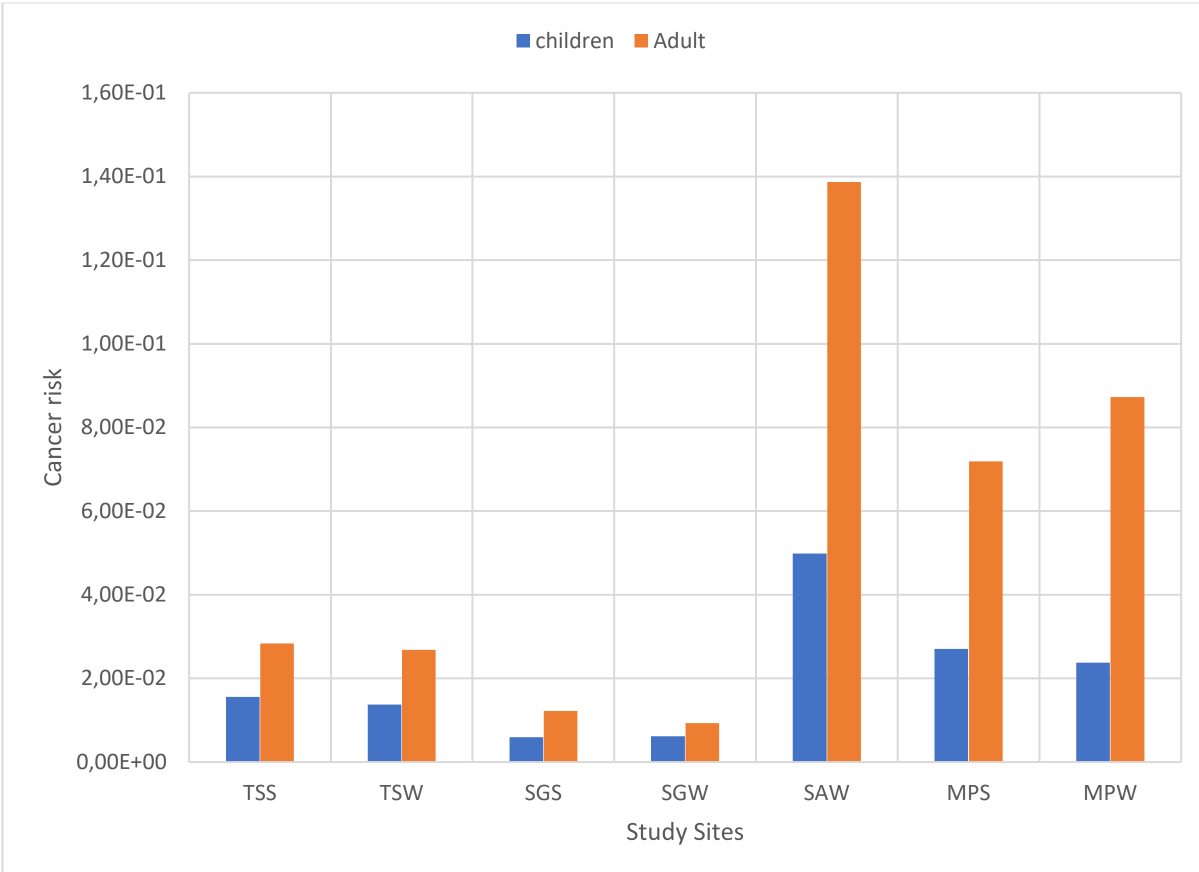


Figure 22: *Cancer risk values of trace metals for adults and9 children in surrounding soil within Soutpansberg*

4.6 Trace metals concentrations from surrounding vegetation

The trace metals from geothermal springs and their surrounding soils were also measured in the vegetation except for Be, As and Se because they are below the detection limit (BDL) of the instrument. Table 21 summarises the mean trace metals concentrations in various parts of different vegetation at specific sites. Generally, vegetation growing on soil has a tendency of absorbing trace metals through its root system and transporting them to other parts of the plant (Otieno *et al.,* 2005; Ojekunle *et al.,* 2014). In addition to the study by Durowoju (2015), this study has shown that geothermal spring water contaminates the surrounding surface soil with trace metals. Since plants depend on soil for their nutrients, there is a high possibility of them absorbing and transmitting these trace metals via their various parts. Also, vegetation has the potential capacity to reduce the concentrations of absorbed trace metals to a harmless state (Phyto-remediation).

Table 24: Mean trace metals concentrations in the surrounding vegetation within Soutpansberg

			V	Cr	Mn	Co	Ni	Cu	Zn	Cd	Sb	Ba	Hg	Pb
Sagole	Amarula	Core	0.489	1.220	12.060	0.372	4.373	2.380	8.297	0.098	0.019	31.300	0.090	0.990
		Leaf	1.034	16.970	50.500	0.462	19.210	21.178	22.090	0.000	0.016	32.380	1.019	0.000
		Bark	1.958	2.901	29.910	0.864	10.605	5.089	10.805	0.052	0.018	39.765	0.115	0.562
	Lowveld mangosteen	Core	0.000	0.477	0.554	0.000	2.406	2.266	11.385	0.000	0.000	2.367	0.000	0.000
		Leaf	0.621	7.842	40.915	0.323	7.506	3.940	43.890	0.000	0.018	6.430	0.319	1.295
		Bark	3.499	6.485	54.860	2.005	14.680	26.390	35.080	0.055	0.024	16.940	0.090	1.597
	leadwood tree	Core	0.488	1.145	15.035	0.475	8.498	3.002	10.031	0.000	0.013	59.305	0.058	0.000
		Leaf	0.412	3.254	66.885	2.313	5.332	6.578	29.650	0.000	0.026	19.915	0.367	0.000
		Bark	1.999	3.653	47.370	1.100	15.315	6.061	12.505	0.000	0.013	96.810	0.089	0.636
Mphephu	Acacia tree	Core	0.266	0.558	9.020	0.137	1.472	1.773	8.509	0.090	0.019	21.510	0.080	0.980
		Leaf	0.515	1.167	81.305	0.238	2.003	8.246	40.935	0.143	0.026	45.290	0.498	0.000
		Bark	0.759	2.672	24.200	0.605	10.308	8.067	27.500	0.117	0.011	54.150	0.075	0.000
	Fig tree	Core	2.128	1.339	3.921	0.057	6.425	2.721	26.160	0.000	0.022	14.755	0.354	0.000
		Leaf	0.644	1.113	29.175	0.228	7.259	6.758	10.892	0.000	0.017	43.130	0.456	0.000
		Bark	1.622	4.396	17.800	0.585	12.755	3.719	13.235	0.000	0.015	68.585	0.000	0.000
	Amarula	Core	0.000	0.340	4.430	0.087	3.453	1.781	8.877	0.000	0.000	38.985	0.000	0.000
		Leaf	23.200	16.565	163.900	5.264	11.820	13.560	31.005	0.000	0.011	82.155	0.195	1.924
		Bark	0.567	1.832	14.880	0.278	3.661	3.048	8.574	0.000	0.011	58.550	0.000	0.000
Tshipise	Suage tree	Core	0.000	0.872	7.919	0.068	2.777	4.760	26.640	0.070	0.012	12.425	0.072	0.727
		Leaf	0.000	0.730	8.828	0.075	5.104	5.486	19.210	0.187	0.011	11.085	0.189	0.000
		Bark	2.711	6.594	29.310	0.514	6.054	10.158	15.010	0.000	0.015	23.875	0.000	0.710
	Amarula	Core	0.000	0.487	6.617	0.128	6.763	3.244	10.760	0.000	0.000	20.760	0.058	0.000
		Leaf	0.323	1.281	22.130	0.290	2.892	2.814	13.300	0.000	0.000	24.885	0.308	0.000
		Bark	0.359	2.054	10.414	0.248	6.055	4.024	10.475	0.000	0.015	20.375	0.000	0.000
	Acacia tree	Core	0.000	0.518	5.376	0.251	5.656	3.273	7.548	0.259	0.017	35.215	0.000	0.000
		Leaf	0.190	1.043	27.520	5.179	4.036	7.294	38.360	0.000	0.012	19.995	0.237	0.000
		Bark	0.326	0.806	5.797	0.428	4.625	3.104	11.375	0.000	0.000	68.775	0.000	0.000
Siloam	Amarula	Core	0.000	0.547	1.112	0.063	4.975	2.105	8.948	0.000	0.000	21.940	0.000	0.000
		Leaf	8.330	4.629	37.200	1.399	4.564	7.857	11.899	0.000	0.016	22.525	0.125	0.000
		Bark	1.056	9.158	29.435	0.371	12.420	9.292	19.125	0.000	0.015	45.350	0.142	0.000
	Guava	Core	0.000	0.477	0.554	0.000	2.406	2.266	11.385	0.000	0.000	2.367	0.000	0.000
		Leaf	0.208	0.605	8.669	0.159	5.683	4.913	17.815	0.462	0.014	26.915	0.000	1.960
		Bark	0.992	1.931	57.075	0.394	12.335	13.855	12.315	0.000	0.016	28.240	0.118	0.000
	Mango	Core	0.000	0.430	2.857	0.023	2.755	1.180	9.545	0.000	0.000	2.653	0.000	0.000
		Leaf	4.480	2.659	40.950	0.989	4.730	5.364	11.190	0.000	0.012	38.030	0.066	0.756
		Bark	0.719	8.332	124.850	0.250	8.743	4.583	13.620	0.061	0.016	39.115	0.111	0.000

Phytoremediation pathway involves phytoextraction, phytodegradation, phytovolatilation, phytostabilisation and phytostimulation of the absorbed trace metals from the soil. Hence, either of the phytoremediation pathways take place in the plant metabolism. The total concentrations of the trace metals in the different parts of vegetation at all the sites showed a similar decreasing trend from the root to the core (that is root-leaf-core). This seems to be the general trend for all plants in the process of their metabolism. This shows that the root system absorbs trace metals from the surrounding soil before transmitting via core to the leaves. The inner core has the lowest concentrations of trace metals because it serves as channel for transpiration compared to bark and leaves that could store before metabolism; except for the Amarula tree at all the sites which shows a contrary trend from the others, with the trend being from leaf to the core (that is a leaf-bark-core). Amarula tree has the largest leaves, and therefore contained more trace elements than its roots.

Statistically, there are significant differences in variances of trace metals concentration from different parts (core, leaves and barks) in Amarula, Lowveld and Leadwood at Sagole ($P < 0.05$). This means that the variations of trace metals concentrations in core, leaves and barks of the plants were significant and not random. Significant variations of trace metals concentrations were observed in two different types of vegetation at Mphephu (Acacia and Fig trees), Tshipise (Sausage tree and Amarula tree) and Siloam (Amarula tree and Mango tree) ($P < 0.05$). However, no significant differences were observed in Amarula, Acacia and Guava trees in Mphephu, Tshipise and Siloam, respectively.

From this study, it can be inferred that the leaf part of the Amarula tree absorb more trace metals than other plant's leaves. However, the bark of mango tree and Leadwood tree also absorb more trace metals than barks of other vegetation. This further confirms the significant variations of the trace metals concentrations among the various parts of the vegetation at different sites.

4.6.1 Uptake efficiency of the trace metals in parts of the vegetation

This study adopts the passive monitoring/observation of analysing trace metals in selected indigenous plants to explore their bioaccumulative/phytoremediative capacity (Ceburnis and Valiulis, 1999). Various plants have been used as bio-indicators to assess the impact of pollution sources in their vicinity due to high metal accumulation in plants (Onder and Dursun, 2006). The percentage uptake of the trace elements core, barks and leaves of the plant were calculated using the formula by Lawal *et al*. (2011):

$$\% \text{ Conc. of uptake} = \text{Conc. of plant's part} \div (\text{Conc. of plant's part} + \text{Conc. of soil}) \times 100$$

The total trace metals concentrations for soil used for the uptake efficiency are 125.30 mg/kg, 260.36 mg/kg, 270.49 mg/kg and 722.89 mg/kg (Table 15) for Sagole, Mphephu, Tshipise and Siloam, respectively. These values were obtained from the average, summation of trace metals analysed in both seasons. The percentage uptake results indicate that different tree species have different uptake capacities with respect to different parts of the tree. The percentage mean trace element uptake by Amarula tree, Lowveld mangosteen and Leadwood trees were 32.99%, 56.82%, 45.03%; 13.44%, 47.44%, 56.34%; 43.90%, 51.81%, 59.69% for inner core, leaves and barks, respectively at Sagole (Figure 23). These species of trees have shown high uptake capacity in this magnitude: Leadwood tree > Amarula tree > Lowveld mangosteen with the leaf and bark as the most absorptive parts. At Mphephu, % uptake by Acacia tree, Fig tree and Amarula tree were 14.57%, 40.92%, 33.04%; 18.19%, 27.68%, 32.03%; 18.21%, 57.31%, 25.98% for inner core, leaves and barks, respectively (Figure 21). The uptake capacity decreases in this magnitude; Amarula tree, Acacia tree and Fig tree. Similarly, the leaves and barks of these species of tree are more absorptive parts. At Tshipise, % uptake by Sausage tree, Amarula tree, Acacia tree was 17.24%, 15.84%, 25.98%; 15.29%, 20.14%, 16.65%; 17.68%, 27.75%, 26.04% for inner core, leaves and barks, respectively (Figure 21). The uptake capacity decreases in this magnitude; Acacia tree, Sausage tree and Amarula trees, respectively. Although, the leaf and bark parts of these species of tree are the most absorptive parts as observed at Sagole and Mphephu but % uptake rate is lower compared to other sites.

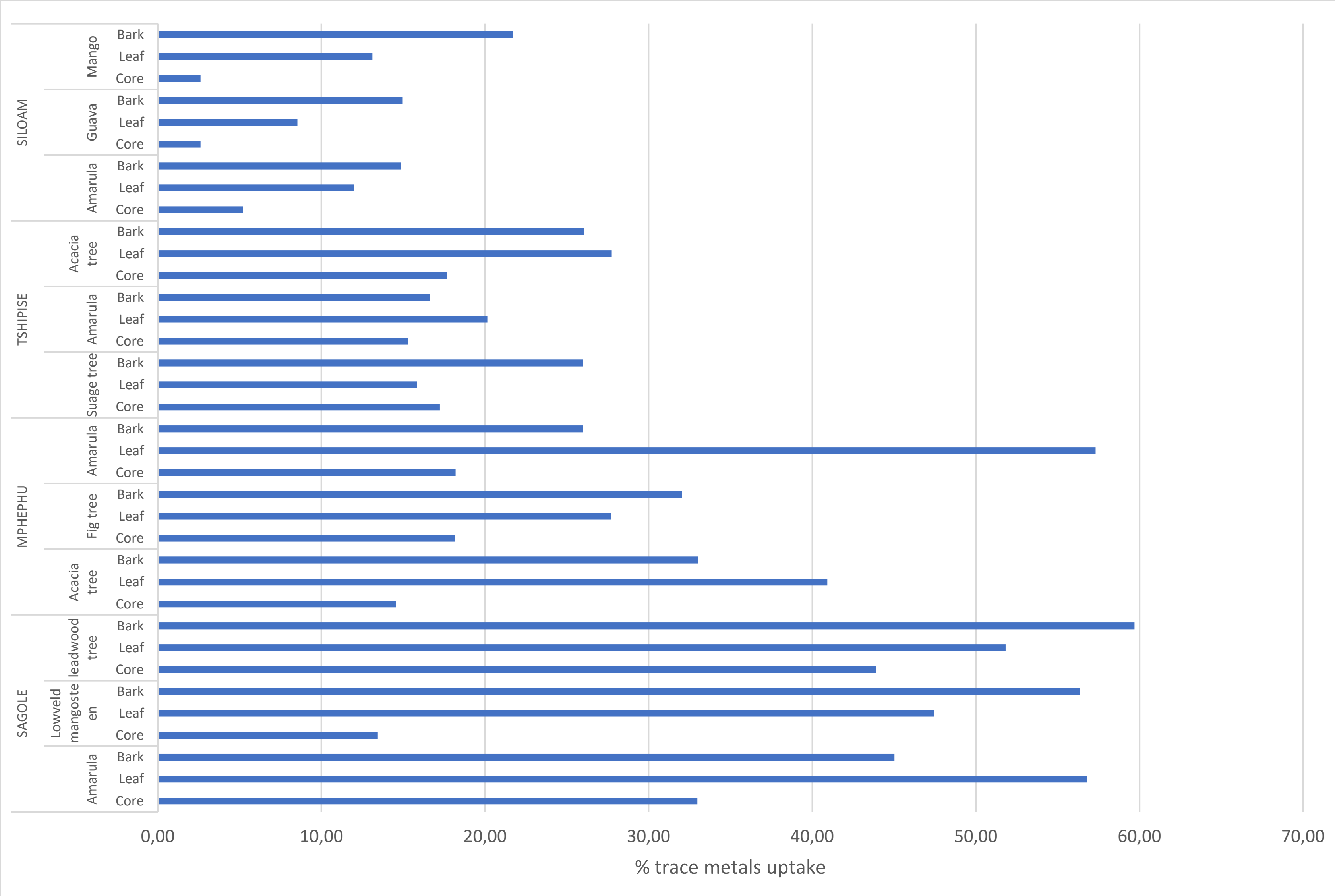


***Figure 23**: Percentage uptake concentrations of the mean trace metal in the vegetation within the Soutpansberg region.*

The percentage uptake by Amarula tree, Guava tree and Mango tree were 5.20%, 12.00%, 14.88%; 2.62%, 8.53%, 14.97%; 2.62%, 13.13%, 21.70% for inner core, leaves and barks, respectively at Siloam (Figure 16). The uptake capacity decreases in this magnitude; Mango tree, Amarula tree and Guava tree. Similarly, the leaves and barks of these species of tree are more absorptive parts. The determination of the percentage uptake ensured the level of bioaccumulation of these trace elements by each tree. All the indigenous trees could be used as bio-indicators to access the level of contamination of trace elements in the soil since their uptake capacity is high. However, the study by Ojekunle *et al*. (2014) showed that mango tree and guava have high uptake capability for some selected heavy metals, which the present study cannot justify. This could be as a result of the broader scope of this study considering about 12 trace metals collectively at four different sites rather than selecting a few elements to evaluate their % uptake individually. This study recommends the use of indigenous trees such as Amarula tree, Acacia tree, Fig tree, mango tree, guava tree, Lowveld mangosteen, Leadwood and Sausage tree for remediation of trace metals contaminated soil. Hence, Amarula tree is selected as the best among others based on its uptake consistency at different sites.

5. Capacity Building

One PhD student participated fully in this project with PhD title "Isotopic signatures and trace metals in geothermal springs and their environmental media within Soutpansberg". Geothermal springs within Soutpansberg (Siloam, Mphephu, Sagole and Tshipise) were studied comprehensively to elucidate on isotopic and trace metals compositions in relation to their surrounding soils and vegetation. This is an eco-hydrological study that shows the interconnectivity of isotopic signatures among water (rainwater, geothermal springs/boreholes), soils and vegetation. The study has shown that rainwater is one of the major components of recharge of geothermal spring, which is isotopically depleted as it infiltrates through the soil. The signatures from soil-water is absorbed by the plant (plant water) and which is evapotranspirated via the leaves and barks to the atmosphere. This study has provided better comprehensive understanding of the geochemical processes, sources, reservoir temperatures and suitability of these geothermal springs. Also, the local meteoric water line was generated, which will be useful for future isotopic research within the locality. Assessment of trace metals concentrations of geothermal springs, surrounding soils and vegetation was carried out; possible health risks associated with these trace metals concentrations in geothermal springs and surrounding soils were assessed in adults and children. The thesis has already generated two published articles;

- Durowoju OS, Odiyo JO and Ekosse GE (2019). Determination of isotopic composition of rainwater to generate local meteoric water line in Thohoyandou, Limpopo Province, South Africa, Water SA, 45(2), DOI: 10.4314/wsa.v45i2.04
- Durowoju OS, Butler M, Ekosse GE and Odiyo JO (2019). Hydrochemical processes and isotopic study of geothermal springs within Soutpansberg, Limpopo Province, South Africa, Applied Sciences, DOI: 10.3390/app9081688

6. Conclusions

Temperature plays a vital and significant role in the geochemical processes of groundwater. Na-Cl and Na-HCO_3 are water types, which are typical of deeper groundwaters (with marine characteristics) which are influenced by the ion-exchange processes. Gibb's plot indicates that rock-water interaction process leads to chemical weathering of the rock-forming minerals. Most of geothermal springs and borehole sources were characterised with high chlorine from the Na-Cl water type, they are affected by geothermal water mixed with saltwater, which is not native water. Whereas, Na-HCO_3-Cl water indicates water rising from periphery of hot granitic source (Siloam). Stable isotopic composition of the geothermal spring and boreholes water confirms that the waters are of meteoric origin with significant role of evaporation and rock-water interaction being the main geochemical processes of the groundwater.

The geothermal springs and boreholes water are not fit for drinking due to high fluoride content, except for the treated water such as water from Tshipise tap water (TTP) and Siloam community tap water (SCC). According to Wilcox (US salinity) diagram, all geothermal and boreholes water samples could be suitable for irrigation purposes. Other indices such as SAR, RSC, PI, and EC showed similar results except for KR and SP, implying that the geothermal springs and boreholes water fall under excellent to good category in both seasons with respect to these parameters. Although, geothermal springs and boreholes water are not fit for drinking due to high fluoride content, they could be used for the following; domestic uses due to its softness, direct heating in refrigeration, green-housing, spa, therapeutic uses, sericulture, concrete curing and coal washing.

Trace metals concentrations of the geothermal springs and boreholes were within permissible drinking guidelines by the SABS and WHO, with exception of Mercury (Hg) which is high in summer season. The bioaccumulation in the human body, however, could result to negative effects. Pearson's correlation reveals that there is a strong relationship between the temperature and pH; and negatively correlated to most of the trace metals. This is an indication of dissolution of minerals (rock-water interaction) under high temperature. HCA and PCA/FA further elucidate the relationship and possible sources of the trace metals. It can be inferred that the rock-water interaction is the main geochemical process governing the formation of trace metals in groundwater. HI values for both children and adults were higher than one and this implies that the communities are at high risk of non-cancer health effects. The ingestion pathway is the major pathway with trace metals such as, Be, Se, Cr, Co, Mn, Hg, V and Zn as the main drivers. As, Cr and Cd were found to be the highest contributors to the potential cancer risk in the study areas with children having a higher risk than adults (Table 25). Therefore, there is need for further clinical study and proper monitoring and control measures to verify actual prevalence of cancer and protect human health, particularly for the children, within the study areas.

The concentrations of the trace metals at different depths of the surrounding soil were found within acceptable limits set by the Department of Environmental Affairs (DEA) except for Cu, Cr, As and Pb at Siloam and Mphephu; Siloam, Tshipise and Mphephu; Sagole; and Siloam, respectively. The relationship of the trace metals and physicochemical parameters was assessed using Pearson's correlation matrix, HCA and PCA/FA. This study shows that trace metals are more soluble in acidic soil and tends to be insoluble in alkaline soil. The sources of trace metals are soil pedogenesis (geogenic), groundwater-surface soil interaction and anthropogenic sources. It was confirmed that ingestion pathway is the major exposure to the surrounding soil at all sites followed by dermal and inhalation pathways. For both children and adult population, the calculated HQ from USEPA model was less than one of the three pathways, which means that there was no significant non-carcinogenic risk in their population. Cr, As and Co were found to be the highest contributors to the potential cancer risk in the selected communities (Table 25). Therefore, the potential cancer risk is high in the general population, that is (1 in 72-162 individuals in child population and 1 in 7-107 individuals for adult population). The ingestion route seems to be the major contributor to excess lifetime potential cancer risk followed by the dermal pathway. Though, the model shows high cancer risk, this cannot be confirmed unless a proper clinical or epidemiological study is conducted.

Table 25: Summarised table for potential non-cancer and cancer health risk calculated from the trace metals concentrations from geothermal springs water and surrounding soils within Soutpansberg.

** - there is potential of occurrence that need for further clinical investigation

	Water				Soil			
	Potential Non-cancer Risk		Potential cancer Risk		Potential Non-cancer Risk		Potential cancer Risk	
	Children	Adults	Children	Adults	Children	Adults	Children	Adults
Be	**	**						
V	**							
Cr	**	**	**	**	**		**	**
Mn	**							
Co							**	**
Ni								
Cu								
Zn								
As	**	**	**	**			**	**
Se	**							
Cd			**	**				
Sb								
Ba								
Hg	**	**						
Pb								

The determination of the percentage uptake ensured the level of bioaccumulation of the trace metals by each indigenous tree. All the indigenous trees could be used as bioindicators to access the level of contamination of trace elements in the soil since their uptake capacity is high. Although, all the indigenous plants are good for remediation of contaminated soils, this study recommended Amarula tree based on its uptake consistency at different sites.

6.1 Recommendations

Proper education should be given to the communities at Siloam, Mphephu, Sagole and Tshipise to caution on the usage of geothermal spring water for domestic and agricultural uses. It is also further recommended that proper care should be taken with exposure and utilisation of the geothermal spring water at Siloam, Mphephu, Sagole and Tshipise. Long-term ingestion of this water could possibly pose a great health risk for the consumers because some of the parameters analysed exceeded the South African water quality standards. Among the parameters of concern are fluoride, nickel, lead and mercury levels. It is therefore recommended that the geothermal spring waters at Siloam, Mphephu, Sagole and Tshipise are monitored on a regular basis, particularly their utilisation. Also, this study is a pointer that recommends a clinical/ecotoxicological study to substantiate these findings. The planting of Amarula tree is more advantageous since its uptake ability is higher than other indigenous trees.

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Appendix 1: Hazard quotient for geothermal springs and boreholes within Soutpansberg

		Hazard Quotient													
		TSS	**TSW**	**SGS**	**SGW**	**MPS**	**MPW**	**SAW**	**SH1**	**SH2**	**BH1**	**BH2**	**SCC**	**TTP**	**HI-total**
							Be								
	Ingestion	1.10E+00	3.50E+00	8.03E-01	5.40E-03	1.56E+00	3.08E+00	3.00E-02	1.92E+00	2.12E+00	2.62E+00	4.06E+00	3.04E+00	5.40E-03	**2.38E+01**
Children	Dermal	-	-	-	-	-	-	-	-	-	-	-	-	-	**-**
	Ingestion	2.46E-02	7.86E-02	1.80E-02	1.21E-04	3.50E-02	6.91E-02	6.73E-04	4.32E-02	4.75E-02	5.88E-02	9.11E-02	6.82E-02	1.21E-04	**5.35E-01**
Adult	Dermal	-	-	-	-	-	-	-	-	-	-	-	-	-	**-**
							V								
	Ingestion	4.37E-01	3.98E-01	3.22E-01	3.47E-01	3.88E-01	3.32E-01	7.64E-02	3.22E-01	4.20E-01	1.22E-01	2.97E-01	4.25E-01	1.10E-01	**4.00E+00**
Children	Dermal	-	-	-	-	-	-	-	-	-	-	-	-	-	**-**
	Ingestion	9.81E-03	8.94E-03	7.22E-03	7.80E-03	8.70E-03	7.46E-03	1.72E-03	7.24E-03	9.42E-03	2.74E-03	6.66E-03	9.53E-03	2.47E-03	**8.97E-02**
Adult	Dermal	-	-	-	-	-	-	-	-	-	-	-	-	-	**-**
							Cr								
	Ingestion	4.98E-01	3.46E-01	4.19E-01	2.66E-01	4.23E-01	3.36E-01	3.60E-03	4.16E-01	4.43E-01	2.80E-01	2.59E-01	4.86E-01	3.61E-01	**4.54E+00**
Children	Dermal	1.83E-03	1.27E-03	1.54E-03	9.74E-04	1.55E-03	1.23E-03	1.32E-05	1.53E-03	1.63E-03	1.03E-03	9.51E-04	1.78E-03	1.32E-03	**1.66E-02**
	Ingestion	1.12E-02	7.76E-03	9.41E-03	5.97E-03	9.49E-03	7.55E-03	8.08E-05	9.34E-03	9.95E-03	6.28E-03	5.82E-03	1.09E-02	8.10E-03	**1.02E-01**
Adult	Dermal	5.31E-05	3.68E-05	4.47E-05	2.83E-05	4.50E-05	3.58E-05	3.84E-07	4.43E-05	4.72E-05	2.98E-05	2.76E-05	5.17E-05	3.85E-05	**4.83E-04**
							Mn								
	Ingestion	1.33E-02	1.11E-02	5.15E-02	1.28E-01	1.83E-01	5.32E-03	1.20E-03	6.27E-03	9.73E-03	5.38E-01	8.28E-03	7.62E-03	7.35E-02	**1.04E+00**
Children	Dermal	8.21E-04	6.84E-04	3.17E-03	7.86E-03	1.13E-02	3.28E-04	7.38E-05	3.86E-04	5.99E-04	3.31E-02	5.09E-04	4.69E-04	4.52E-03	**6.38E-02**
	Ingestion	2.99E-04	2.50E-04	1.16E-03	2.87E-03	4.11E-03	1.19E-04	2.69E-05	1.41E-04	2.18E-04	1.21E-02	1.86E-04	1.71E-04	1.65E-03	**2.33E-02**
Adult	Dermal	2.38E-05	1.99E-05	9.21E-05	2.28E-04	3.27E-04	9.52E-06	2.15E-06	1.12E-05	1.74E-05	9.61E-04	1.48E-05	1.36E-05	1.31E-04	**1.85E-03**
							Co								
	Ingestion	1.26E-03	1.67E-03	2.59E-03	2.13E-03	1.75E-03	2.19E-03	2.40E-04	1.12E-03	1.57E-03	2.05E-02	3.05E-03	1.43E-03	1.02E-03	**4.05E-02**
Children	Dermal	1.62E-02	2.15E-02	3.33E-02	2.75E-02	2.25E-02	2.81E-02	3.09E-03	1.44E-02	2.01E-02	2.64E-01	3.92E-02	1.84E-02	1.31E-02	**5.21E-01**
	Ingestion	2.82E-05	3.75E-05	5.82E-05	4.79E-05	3.92E-05	4.91E-05	5.39E-06	2.51E-05	3.52E-05	4.61E-04	6.84E-05	3.21E-05	2.29E-05	**9.10E-04**
Adult	Dermal	4.69E-04	6.25E-04	9.69E-04	7.98E-04	6.53E-04	8.17E-04	8.97E-05	4.17E-04	5.85E-04	7.67E-03	1.14E-03	5.34E-04	3.81E-04	**1.52E-02**

Ni															
	Ingestion	1.35E-02	1.58E-02	5.95E-03	6.63E-03	1.28E-02	5.06E-03	4.26E-03	4.90E-03	8.89E-03	7.51E-02	3.27E-03	1.13E-02	9.43E-03	**1.77E-01**
Children	Dermal	1.08E-08	1.26E-08	4.75E-09	5.30E-09	1.02E-08	4.04E-09	3.40E-09	3.92E-09	7.11E-09	6.00E-08	2.61E-09	9.03E-09	7.53E-09	**1.41E-07**
	Ingestion	3.02E-04	3.55E-04	1.34E-04	1.49E-04	2.88E-04	1.13E-04	9.56E-05	1.10E-04	2.00E-04	1.69E-03	7.34E-05	2.54E-04	2.12E-04	**3.97E-03**
Adult	Dermal	5.13E-06	6.02E-06	2.26E-06	2.52E-06	4.88E-06	1.92E-06	1.62E-06	1.87E-06	3.38E-06	2.86E-05	1.24E-06	4.30E-06	3.59E-06	**6.73E-05**
Cu															
	Ingestion	3.88E-02	6.08E-02	9.92E-02	2.08E-04	4.15E-03	2.92E-05	1.14E-03	2.92E-05	5.96E-03	1.02E-01	1.12E-03	6.98E-03	1.56E-02	**3.36E-01**
Children	Dermal	2.19E-04	3.44E-04	5.61E-04	1.18E-06	2.35E-05	1.65E-07	6.42E-06	1.65E-07	3.37E-05	5.75E-04	6.31E-06	3.94E-05	8.83E-05	**1.90E-03**
	Ingestion	8.71E-04	1.37E-03	2.23E-03	4.67E-06	9.32E-05	6.55E-07	2.55E-05	6.55E-07	1.34E-04	2.29E-03	2.50E-05	1.57E-04	3.51E-04	**7.54E-03**
Adult	Dermal	6.37E-06	9.99E-06	1.63E-05	3.42E-08	6.82E-07	4.79E-09	1.86E-07	4.79E-09	9.80E-07	1.67E-05	1.83E-07	1.15E-06	2.57E-06	**5.52E-05**
Zn															
	Ingestion	1.25E-01	1.86E-01	1.18E-01	7.78E-02	1.97E-02	8.40E-03	3.80E-04	3.60E-06	3.60E-06	1.40E-01	3.60E-06	3.60E-06	1.79E-02	**6.94E-01**
Children	Dermal	1.84E-03	2.73E-03	1.73E-03	1.14E-03	2.90E-04	1.23E-04	5.57E-06	5.28E-08	5.28E-08	2.06E-03	5.28E-08	5.28E-08	2.63E-04	**1.02E-02**
	Ingestion	7.30E-04	2.34E-03	5.35E-04	3.60E-06	1.04E-03	2.05E-03	2.00E-05	1.28E-03	1.41E-03	1.75E-03	2.70E-03	2.02E-03	3.60E-06	**1.59E-02**
Adult	Dermal	5.33E-05	7.92E-05	5.02E-05	3.32E-05	8.41E-06	3.58E-06	1.62E-07	1.53E-09	1.53E-09	5.98E-05	1.53E-09	1.53E-09	7.65E-06	**2.96E-04**
As															
	Ingestion	8.17E-01	8.05E-01	5.41E-01	7.89E-01	1.09E+00	8.39E-01	4.04E-01	4.13E-01	1.22E+00	7.68E-01	5.18E-01	1.22E+00	5.20E-01	**9.94E+00**
Children	Dermal	2.99E-03	2.95E-03	1.98E-03	2.89E-03	3.99E-03	3.07E-03	1.48E-03	1.51E-03	4.46E-03	2.82E-03	1.90E-03	4.47E-03	1.91E-03	**3.64E-02**
	Ingestion	1.83E-02	1.81E-02	1.21E-02	1.77E-02	2.44E-02	1.88E-02	9.07E-03	9.27E-03	2.73E-02	1.72E-02	1.16E-02	2.74E-02	1.17E-02	**2.23E-01**
Adult	Dermal	8.70E-05	8.58E-05	5.77E-05	8.41E-05	1.16E-04	8.93E-05	4.30E-05	4.40E-05	1.30E-04	8.18E-05	5.51E-05	1.30E-04	5.54E-05	**1.06E-03**
Se															
	Ingestion	1.40E-01	1.48E-01	9.25E-02	1.38E-01	2.41E-01	1.54E-01	1.63E-02	1.22E-01	2.63E-01	1.40E-01	8.68E-02	2.63E-01	7.79E-02	**1.88E+00**
Children	Dermal	-	-	-	-	-	-	-	-	-	-	-	-	-	**-**
	Ingestion	3.14E-03	3.33E-03	2.08E-03	3.09E-03	5.40E-03	3.46E-03	3.66E-04	2.73E-03	5.90E-03	3.15E-03	1.95E-03	5.89E-03	1.75E-03	**4.22E-02**
-	Dermal	-	-	-	-	-	-	-	-	-	-	-	-	-	**-**
Cd															
	Ingestion	6.76E-03	2.94E-03	1.60E-03	6.46E-03	9.20E-04	1.65E-02	2.40E-03	1.08E-03	8.40E-04	8.71E-02	1.08E-03	8.40E-04	5.40E-03	**1.34E-01**
Children	Dermal	2.48E-05	1.08E-05	5.87E-06	2.37E-05	3.37E-06	6.05E-05	8.80E-06	3.96E-06	3.08E-06	3.19E-04	3.96E-06	3.08E-06	1.98E-05	**4.91E-04**
	Ingestion	1.52E-04	6.60E-05	3.59E-05	1.45E-04	2.07E-05	3.70E-04	5.39E-05	2.42E-05	1.89E-05	1.96E-03	2.42E-05	1.89E-05	1.21E-04	**3.01E-03**
Adult	Dermal	7.20E-07	3.13E-07	1.70E-07	6.88E-07	9.80E-08	1.76E-06	2.56E-07	1.15E-07	8.95E-08	9.28E-06	1.15E-07	8.95E-08	5.75E-07	**1.43E-05**

							Sb								
	Ingestion	1.59E-02	6.60E-03	9.40E-03	1.76E-02	1.07E-02	5.18E-02	9.00E-03	1.50E-03	4.50E-03	3.66E-02	2.37E-02	2.70E-03	2.85E-02	**2.18E-01**
Children	Dermal	-	-	-	-	-	-	-	-	-	-	-	-	-	**-**
	Ingestion	3.57E-04	1.48E-04	2.11E-04	3.96E-04	2.40E-04	1.16E-03	2.02E-04	3.37E-05	1.01E-04	8.22E-04	5.32E-04	6.06E-05	6.40E-04	**4.90E-03**
Adult	Dermal	-	-	-	-	-	-	-	-	-	-	-	-	-	**-**
							Ba								
	Ingestion	9.22E-04	1.58E-02	4.68E-04	2.54E-02	5.28E-03	1.74E-02	6.25E-03	2.27E-04	4.32E-03	4.04E-02	4.32E-02	4.10E-03	5.40E-06	**1.64E-01**
Children	Dermal	-	-	-	-	-	-	-	-	-	-	-	-	-	**-**
	Ingestion	2.07E-05	3.55E-04	1.05E-05	5.71E-04	1.18E-04	3.91E-04	1.40E-04	5.10E-06	9.70E-05	9.07E-04	9.70E-04	9.21E-05	1.21E-07	**3.68E-03**
Adult	Dermal	-	-	-	-	-	-	-	-	-	-	-	-	-	**-**
							Hg								
	Ingestion	2.44E+00	2.48E-01	1.30E+00	1.61E-01	7.27E-01	1.72E-01	1.40E-01	2.65E-01	3.19E-01	6.12E-02	6.40E-01	1.84E-01	2.88E-01	**6.95E+00**
Children	Dermal	8.96E-03	9.11E-04	4.78E-03	5.90E-04	2.67E-03	6.31E-04	5.13E-04	9.71E-04	1.17E-03	2.24E-04	2.35E-03	6.75E-04	1.06E-03	**2.55E-02**
	Ingestion	5.49E-02	5.58E-03	2.93E-02	3.62E-03	1.63E-02	3.87E-03	3.14E-03	5.94E-03	7.17E-03	1.37E-03	1.44E-02	4.13E-03	6.47E-03	**1.56E-01**
Adult	Dermal	2.60E-04	2.65E-05	1.39E-04	1.72E-05	7.74E-05	1.83E-05	1.49E-05	2.82E-05	3.40E-05	6.52E-06	6.81E-05	1.96E-05	3.07E-05	**7.41E-04**
							Pb								
	Ingestion	9.67E-03	1.12E-02	1.68E-02	3.09E-04	3.09E-04	3.09E-04	3.09E-03	5.86E-03	3.09E-04	3.09E-04	3.09E-04	3.09E-04	2.19E-03	**5.09E-02**
Children	Dermal	2.36E-04	2.73E-04	4.10E-04	7.54E-06	7.54E-06	7.54E-06	7.54E-05	1.43E-04	7.54E-06	7.54E-06	7.54E-06	7.54E-06	5.36E-05	**1.24E-03**
	Ingestion	2.17E-04	2.51E-04	3.77E-04	6.93E-06	6.93E-06	6.93E-06	6.93E-05	1.32E-04	6.93E-06	6.93E-06	6.93E-06	6.93E-06	4.93E-05	**1.14E-03**
Adult	Dermal	6.87E-06	7.94E-06	1.19E-05	2.19E-07	2.19E-07	2.19E-07	2.19E-06	4.16E-06	2.19E-07	2.19E-07	2.19E-07	2.19E-07	1.56E-06	**3.62E-05**

Appendix 2: Statistical summary of the trace metals concentrations from the surrounding soil of the geothermal springs

		Tshipise S	Tshipise W	Mphephu S	Mphephu W	Sagole S	Sagole W	Siloam
pH	Min	7.50	8.01	6.62	7.47	3.10	9.31	6.67
	Max	8.55	8.05	6.97	7.76	9.90	9.72	7.15
	Mean	8.12	8.04	6.80	7.62	7.38	9.45	6.91
	SD	0.55	0.02	0.25	0.21	3.73	.23	0.34
	CV	6.79	0.29	3.64	2.69	50.49	2.45	4.91
EC	Min	89.40	90.10	111.20	27.40	124.10	165.80	90.60
	Max	253.90	130.20	217.50	40.80	1441.00	376.00	116.90
	Mean	165.83	105.37	164.35	34.10	846.03	275.17	103.75
	SD	82.86	21.69	75.17	9.48	667.57	92.00	18.60
	CV	49.97	20.59	45.73	27.79	78.91	33.43	17.92
TDS	Min	57.20	57.60	71.10	17.50	79.40	125.00	58.00
	Max	162.00	613.00	139.00	26.10	922.00	241.00	74.80
	Mean	105.97	251.30	105.05	21.80	541.47	176.00	66.40
	SD	52.78	313.50	48.01	6.08	427.18	59.25	11.88
	CV	49.80	124.75	45.70	27.90	78.89	33.67	17.89
Be	Min	0.14	0.21	0.34	0.20	0.05	0.04	0.59
	Max	0.21	0.30	0.63	0.31	0.75	0.09	0.64
	Mean	0.18	0.25	0.48	0.26	0.30	0.06	0.62
	SD	0.04	0.05	0.20	0.08	0.39	0.03	0.04
	CV	21.05	18.68	42.44	31.61	128.10	42.33	6.32
V	Min	12.24	16.82	58.50	48.14	4.15	4.13	165.10
	Max	17.13	25.23	68.17	49.02	7.02	6.53	172.40
	Mean	15.25	20.11	63.34	48.58	6.01	5.35	168.75
	SD	2.64	4.50	6.84	0.62	1.61	1.20	5.16
	CV	17.28	22.36	10.80	1.28	26.81	22.44	3.06
Cr	Min	37.93	36.93	35.32	27.92	3.77	4.71	90.54
	Max	46.23	44.90	36.10	38.38	9.98	7.81	96.35
	Mean	42.34	39.78	35.71	33.15	6.08	6.59	93.45
	SD	4.17	4.45	0.55	7.40	3.40	1.66	4.11
	CV	9.86	11.18	1.54	22.31	55.87	25.13	4.40
Mn	Min	99.98	120.30	35.41	46.96	18.07	24.59	118.30
	Max	144.00	157.10	47.22	71.84	68.76	53.96	119.00
	Mean	119.06	135.90	41.32	59.40	39.98	36.23	118.65
	SD	22.59	19.03	8.35	17.59	26.03	15.60	0.49
	CV	18.97	14.00	21.21	29.62	65.12	43.06	0.42
Co	Min	3.62	4.61	13.80	19.12	0.89	1.00	28.66
	Max	5.28	7.78	14.66	21.52	2.29	1.52	28.67
	Mean	4.66	5.78	14.23	20.32	1.77	1.21	28.67
	SD	0.91	1.74	0.61	1.70	0.77	0.27	0.01
	CV	19.44	30.06	4.27	8.35	43.38	22.46	0.02
Ni	Min	24.46	26.10	15.72	11.60	2.41	3.41	51.65
	Max	34.44	37.03	21.10	21.45	11.27	6.13	57.39
	Mean	5.14	29.99	18.41	.16.53	6.00	4.66	54.52
	SD	30.16	6.11	3.80	6.97	4.66	1.3	4.06
	CV	17.04	20.37	20.66	42.15	77.74	29.53	7.44
Cu	Min	8.52	13.73	25.09	19.30	8.11	5.63	97.07

	Max	12.70	19.13	33.45	25.39	9.23	7.14	103.60
	Mean	11.13	15.97	29.27	22.35	8.67	6.19	100.34
	SD	2.27	2.82	5.91	4.31	0.56	0.83	4.62
	CV	20.44	17.63	20.20	19.27	6.46	13.40	4.60
Zn	Min	14.16	1549	15.52	8.08	2.51	3.83	48.62
	Max	15.75	21.25	37.74	19.77	17.17	6.10	48.94
	Mean	15.05	17.63	26.63	13.93	10.11	4.95	48.78
	SD	0.81	3.15	15.71	8.26	7.34	1.14	0.23
	CV	5.39	17.88	59.00	59.35	72.66	22.99	0.46
As	Min	0.22	0.37	0.44	0.10	0.33	0.26	0.79
	Max	0.38	0.93	1.10	0.67	7.41	0.59	0.79
	Mean	0.30	0.66	0.77	0.39	2.69	0.39	0.79
	SD	0.08	0.28	0.47	0.40	4.08	0.17	0.00
	CV	26.32	42.46	61.16	103.64	151.66	43.82	0.63
Se	Min	0.09	0.18	0.36	0.11	0.07	0.00	0.25
	Max	0.27	0.18	1.53	0.33	0.14	0.10	0.26
	Mean	0.15	0.18	0.95	0.22	0.10	0.06	0.26
	SD	0.10	0.00	0.83	0.15	0.04	0.05	0.01
	CV	68.25	1.40	87.66	69.13	35.33	86..07	3.29
Cd	Min	0.02	0.02	0.04	0.02	0.01	0.01	0.26
	Max	0.04	0.04	0.09	0.04	0.02	0.02	0.36
	Mean	0.03	0.03	0.07	0.03	0.01	0.01	0.31
	SD	0.01	0.01	0.04	0.01	0.01	0.01	0.07
	CV	28.23	19.20	56.99	48.85	43.83	50.62	23.03
Sb	Min	0.01	0.02	0.02	0.01	0.02	0.01	0.02
	Max	0.02	0.04	0.04	0.01	0.30	0.02	0.03
	Mean	0.01	0.03	0.03	0.01	0.11	0.01	0.03
	SD	0.00	0.01	0.01	0.00	0.16	0.00	0.00
	CV	14.19	27.45	52.38	18.45	141.51	31.49	19.41
Ba	Min	11.09	14.51	23.80	18.03	3.17	3.44	48.40
	Max	13.88	20.81	45.36	41.58	253.20	19.87	51.48
	Mean	12.42	17.18	34.58	29.81	88.97	9.67	49.94
	SD	1.40	3.26	15.25	16.65	142.28	8.91	2.18
	CV	11.27	18.95	44.09	55.87	159.91	92.17	4.36
Hg	Min	0.11	0.03	0.00	0.00	0.00	0.00	0.00
	Max	0.23	0.29	0.01	0.00	0.12	0.04	0.00
	Mean	0.16	013	0.00	0.00	0.05	0.02	0.00
	SD	0.06	0.14	0.00	0.00	0.06	0.02	0.00
	CV	38.91	112.47	94.28	0.00	139.94	161.66	0.00
Pb	Min	2.00	2.96	4.08	2.96	1.43	1.15	30.60
	Max	2.42	5.74	9.45	3.51	6.08	1.49	85.02
	Mean	2.26	4.20	6.77	3.24	3.08	1.26	57.81
	SD	0.23	1.42	3.80	0.39	2.60	0.19	38.48
	CV	10.10	33.75	56.18	11.95	84.45	15.35	66.56

Appendix 3: Hazard quotient (Cancer) for surrounding soils of the geothermal springs within Soutpansberg

	Be						V						Cr					
	Ingestion		Inhalation		Dermal		Ingestion		Inhalation		Dermal		Ingestion		Inhalation		Dermal	
	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults
TSS	1.20E-02	1.29E-03	3.30E-07	1.42E-07	-	-	4.35E-02	4.66E-03	1.19E-06	5.12E-07	-	-	1.97E-01	2.11E-02	5.41E-04	2.32E-04	4.14E-04	8.57E-04
TSW	1.44E-02	1.55E-03	3.97E-07	1.70E-07	-	-	4.63E-02	4.97E-03	1.27E-06	5.46E-07	-	-	1.60E-01	1.71E-02	4.39E-04	1.88E-04	3.36E-04	6.95E-04
SGS	7.03E-03	7.53E-04	1.93E-07	8.28E-08	-	-	1.74E-02	1.87E-03	4.78E-07	2.05E-07	-	-	4.25E-02	4.56E-03	1.17E-04	5.01E-05	8.93E-05	1.85E-04
SGW	5.95E-03	6.37E-04	1.63E-07	7.00E-08	-	-	1.66E-02	1.78E-03	4.55E-07	1.95E-07	-	-	3.33E-02	3.57E-03	9.14E-05	3.92E-05	6.99E-05	1.45E-04
SAW	3.76E-02	4.03E-03	1.03E-06	4.43E-07	-	-	4.19E-01	4.49E-02	1.15E-05	4.93E-06	-	-	3.86E-01	4.13E-02	1.06E-03	4.54E-04	8.10E-04	1.68E-03
MPS	4.00E-02	4.29E-03	1.10E-06	4.71E-07	-	-	1.73E-01	1.85E-02	4.75E-06	2.04E-06	-	-	1.54E-01	1.65E-02	4.23E-04	1.81E-04	3.23E-04	6.69E-04
MPW	1.27E-02	1.36E-03	3.48E-07	1.49E-07	-	-	1.24E-01	1.33E-02	3.42E-06	1.46E-06	-	-	1.19E-01	1.27E-02	3.27E-04	1.40E-04	2.50E-04	5.18E-04
	Mn						Co						Ni					
	Ingestion		Inhalation		Dermal		Ingestion		Inhalation		Dermal		Ingestion		Inhalation		Dermal	
	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults
TSS	6.03E-02	6.46E-03	1.66E-06	7.10E-07	2.13E-03	4.40E-03	3.25E-03	3.48E-04	3.13E-05	1.34E-05	2.39E-03	4.96E-03	2.20E-02	2.36E-03	6.05E-07	2.59E-07	1.65E-04	3.42E-04
TSW	6.94E-02	7.44E-03	1.91E-06	8.17E-07	2.45E-03	5.07E-03	3.17E-03	3.40E-04	3.06E-05	1.31E-05	2.34E-03	4.84E-03	1.67E-02	1.79E-03	4.58E-07	1.96E-07	1.25E-04	2.59E-04
SGS	3.66E-02	3.92E-03	1.01E-06	4.31E-07	1.29E-03	2.67E-03	1.47E-03	1.57E-04	1.41E-05	6.06E-06	1.08E-03	2.24E-03	7.20E-03	7.72E-04	1.98E-07	8.48E-08	5.40E-05	1.12E-04
SGW	2.87E-02	3.08E-03	7.90E-07	3.38E-07	1.01E-03	2.10E-03	9.70E-04	1.04E-04	9.35E-06	4.01E-06	7.15E-04	1.48E-03	3.92E-03	4.20E-04	1.08E-07	4.61E-08	2.94E-05	6.09E-05
SAW	6.30E-02	6.75E-03	1.73E-06	7.42E-07	2.22E-03	4.60E-03	1.83E-02	1.96E-03	1.77E-04	7.57E-05	1.35E-02	2.80E-02	3.30E-02	3.54E-03	9.07E-07	3.89E-07	2.48E-04	5.13E-04
MPS	1.89E-02	2.02E-03	5.18E-07	2.22E-07	6.65E-04	1.38E-03	9.37E-03	1.00E-03	9.03E-05	3.87E-05	6.91E-03	1.43E-02	1.35E-02	1.45E-03	3.71E-07	1.59E-07	1.01E-04	2.10E-04
MPW	2.50E-02	2.68E-03	6.87E-07	2.95E-07	8.82E-04	1.83E-03	1.22E-02	1.31E-03	1.18E-04	5.05E-05	9.01E-03	1.87E-02	7.42E-03	7.95E-04	2.04E-07	8.73E-08	5.56E-05	1.15E-04
	Cu						Zn						As					
	Ingestion		Inhalation		Dermal		Ingestion		Inhalation		Dermal		Ingestion		Inhalation		Dermal	
	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults
TSS	4.39E-03	4.70E-04	1.21E-07	5.17E-08	1.42E-05	2.94E-05	6.49E-04	6.96E-05	1.78E-08	7.65E-09	5.46E-06	1.13E-05	1.63E-02	1.74E-03	4.47E-07	1.92E-07	3.42E-05	7.08E-05
TSW	4.74E-03	5.08E-04	1.30E-07	5.59E-08	1.54E-05	3.18E-05	6.88E-04	7.37E-05	1.89E-08	8.10E-09	5.78E-06	1.20E-05	1.57E-02	1.68E-03	4.32E-07	1.85E-07	3.30E-05	6.84E-05
SGS	3.00E-03	3.22E-04	8.25E-08	3.53E-08	9.72E-06	2.01E-05	7.32E-04	7.84E-05	2.01E-08	8.62E-09	6.15E-06	1.27E-05	1.42E-02	1.52E-03	3.90E-07	1.67E-07	2.98E-05	6.17E-05
SGW	2.47E-03	2.64E-04	6.78E-08	2.91E-08	7.99E-06	1.65E-05	2.10E-04	2.25E-05	5.77E-09	2.47E-09	1.76E-06	3.66E-06	2.50E-02	2.68E-03	6.87E-07	2.95E-07	5.25E-05	1.09E-04
SAW	3.35E-02	3.59E-03	9.22E-07	3.95E-07	1.09E-04	2.25E-04	2.07E-03	2.22E-04	5.69E-08	2.44E-08	1.74E-05	3.61E-05	3.35E-02	3.59E-03	9.21E-07	3.95E-07	7.04E-05	1.46E-04
MPS	1.16E-02	1.24E-03	3.18E-07	1.36E-07	3.74E-05	7.75E-05	1.61E-03	1.72E-04	4.42E-08	1.89E-08	1.35E-05	2.80E-05	4.68E-02	5.01E-03	1.29E-06	5.51E-07	9.83E-05	2.04E-04
MPW	6.67E-03	7.15E-04	1.83E-07	7.85E-08	2.16E-05	4.47E-05	3.44E-04	3.69E-05	9.46E-09	4.06E-09	2.89E-06	5.99E-06	4.39E-03	4.70E-04	1.21E-07	5.17E-08	9.22E-06	1.91E-05

	Se						Cd						Sb					
	Ingestion		Inhalation		Dermal		Ingestion		Inhalation		Dermal		Ingestion		Inhalation		Dermal	
	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults
TSS	6.90E-04	7.40E-05	1.90E-08	8.13E-09	-	-	4.35E-04	4.66E-05	2.10E-07	8.98E-08	9.13E-07	1.89E-06	4.47E-04	4.79E-05	1.23E-08	5.27E-09	-	-
TSW	4.53E-04	4.85E-05	1.24E-08	5.33E-09	-	-	3.07E-04	3.29E-05	1.48E-07	6.34E-08	6.44E-07	1.33E-06	6.71E-04	7.19E-05	1.84E-08	7.90E-09	-	-
SGS	1.79E-04	1.92E-05	4.92E-09	2.11E-09	-	-	2.81E-04	3.01E-05	1.36E-07	5.81E-08	5.91E-07	1.22E-06	6.07E-04	6.51E-05	1.67E-08	7.15E-09	-	-
SGW	2.51E-04	2.68E-05	6.88E-09	2.95E-09	-	-	1.28E-04	1.37E-05	6.16E-08	2.64E-08	2.68E-07	5.56E-07	6.39E-04	6.85E-05	1.76E-08	7.53E-09	-	-
SAW	6.75E-04	7.23E-05	1.85E-08	7.95E-09	-	-	3.29E-03	3.52E-04	1.58E-06	6.79E-07	6.90E-06	1.43E-05	9.27E-04	9.93E-05	2.55E-08	1.09E-08	-	-
MPS	3.92E-03	4.20E-04	1.08E-07	4.62E-08	-	-	1.20E-03	1.29E-04	5.79E-07	2.48E-07	2.52E-06	5.23E-06	1.18E-03	1.27E-04	3.25E-08	1.39E-08	-	-
MPW	2.92E-04	3.12E-05	8.01E-09	3.43E-09	-	-	2.30E-04	2.47E-05	1.11E-07	4.75E-08	4.83E-07	1.00E-06	3.20E-04	3.42E-05	8.78E-09	3.76E-09	-	-
	Ba						**Hg**						**Pb**					
	Ingestion		Inhalation		Dermal		Ingestion		Inhalation		Dermal		Ingestion		Inhalation		Dermal	
	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults
TSS	7.86E-04	8.42E-05	2.16E-08	9.25E-09	-	-	9.76E-03	1.05E-03	9.35E-07	4.01E-07	2.05E-05	4.25E-05	8.61E-03	9.23E-04	2.37E-07	1.01E-07	1.21E-04	2.50E-04
TSW	9.28E-04	9.94E-05	2.55E-08	1.09E-08	-	-	2.81E-03	3.01E-04	2.70E-07	1.16E-07	5.91E-06	1.22E-05	1.08E-02	1.16E-03	2.97E-07	1.27E-07	1.51E-04	3.13E-04
SGS	6.74E-04	7.22E-05	1.85E-08	7.93E-09	-	-	5.03E-03	5.39E-04	4.82E-07	2.07E-07	1.06E-05	2.19E-05	2.22E-02	2.38E-03	6.11E-07	2.62E-07	3.11E-04	6.45E-04
SGW	1.27E-03	1.36E-04	3.49E-08	1.50E-08	-	-	4.26E-05	4.57E-06	4.08E-09	1.75E-09	8.95E-08	1.85E-07	5.43E-03	5.82E-04	1.49E-07	6.39E-08	7.60E-05	1.57E-04
SAW	3.09E-03	3.32E-04	8.50E-08	3.64E-08	-	-	4.26E-05	4.57E-06	4.08E-09	1.75E-09	8.95E-08	1.85E-07	3.11E-01	3.33E-02	8.53E-06	3.66E-06	4.35E-03	9.01E-03
MPS	2.90E-03	3.11E-04	7.97E-08	3.41E-08	-	-	2.13E-04	2.28E-05	2.04E-08	8.75E-09	4.47E-07	9.27E-07	3.45E-02	3.70E-03	9.49E-07	4.07E-07	4.83E-04	1.00E-03
MPW	1.15E-03	1.23E-04	3.17E-08	1.36E-08	-	-	4.26E-05	4.57E-06	4.08E-09	1.75E-09	8.95E-08	1.85E-07	1.08E-02	1.16E-03	2.97E-07	1.27E-07	1.52E-04	3.14E-04

Appendix 4: Hazard quotient (Cancer) for surrounding soils of the geothermal springs within Soutpansberg

	Be						V						Cr					
	Ingestion		inhalation		dermal		Ingestion		inhalation		dermal		Ingestion		inhalation		dermal	
	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults
TSS	1.03E-03	5.52E-04	2.83E-08	6.06E-08	-	-	3.72E-03	2.00E-04	1.02E-07	2.19E-08	-	-	1.69E-02	9.05E-03	4.64E-05	9.94E-06	3.55E-05	3.67E-04
TSW	1.24E-03	6.63E-04	3.40E-08	7.29E-08	-	-	3.97E-03	2.13E-04	1.09E-07	2.34E-08	-	-	1.37E-02	7.34E-03	3.76E-05	8.06E-06	2.88E-05	2.98E-04
SGS	6.03E-04	3.23E-04	1.66E-08	3.55E-08	-	-	1.49E-03	8.00E-05	4.10E-08	8.79E-09	-	-	3.64E-03	1.95E-03	1.00E-05	2.15E-06	7.65E-06	7.93E-05
SGW	5.10E-04	2.73E-04	1.40E-08	3.00E-08	-	-	1.42E-03	7.61E-05	3.90E-08	8.36E-09	-	-	2.85E-03	1.53E-03	7.84E-06	1.68E-06	5.99E-06	6.21E-05
SAW	3.22E-03	1.73E-03	8.85E-08	1.90E-07	-	-	3.59E-02	1.92E-03	9.86E-07	2.11E-07	-	-	3.31E-02	1.77E-02	9.09E-05	1.95E-05	6.95E-05	7.19E-04
MPS	3.43E-03	1.84E-03	9.42E-08	2.02E-07	-	-	1.48E-02	7.94E-04	4.07E-07	8.73E-08	-	-	1.32E-02	7.06E-03	3.62E-05	7.76E-06	2.77E-05	2.87E-04
MPW	1.08E-03	5.81E-04	2.98E-08	6.39E-08	-	-	1.07E-02	5.71E-04	2.93E-07	6.27E-08	-	-	1.02E-02	5.46E-03	2.80E-05	6.00E-06	2.14E-05	2.22E-04
	Mn						Co						Ni					
TSS	5.17E-03	2.77E-03	1.42E-07	3.04E-07	1.82E-04	1.89E-03	2.79E-04	1.49E-04	2.69E-06	5.75E-06	2.05E-04	2.13E-03	1.89E-03	1.01E-03	5.18E-08	1.11E-07	1.42E-05	1.47E-04
TSW	5.95E-03	3.19E-03	1.63E-07	3.50E-07	2.10E-04	2.17E-03	2.72E-04	1.46E-04	2.62E-06	5.61E-06	2.00E-04	2.07E-03	1.43E-03	7.66E-04	3.93E-08	8.42E-08	1.07E-05	1.11E-04
SGS	3.14E-03	1.68E-03	8.63E-08	1.85E-07	1.11E-04	1.15E-03	1.26E-04	6.73E-05	1.21E-06	2.60E-06	9.26E-05	9.59E-04	6.18E-04	3.31E-04	1.70E-08	3.64E-08	4.63E-06	4.80E-05
SGW	2.46E-03	1.32E-03	6.77E-08	1.45E-07	8.68E-05	8.99E-04	8.32E-05	4.46E-05	8.02E-07	1.72E-06	6.13E-05	6.35E-04	3.36E-04	1.80E-04	9.23E-09	1.98E-08	2.52E-06	2.61E-05
SAW	5.40E-03	2.89E-03	1.48E-07	3.18E-07	1.90E-04	1.97E-03	1.57E-03	8.41E-04	1.51E-05	3.24E-05	1.16E-03	1.20E-02	2.83E-03	1.52E-03	7.78E-08	1.67E-07	2.12E-05	2.20E-04
MPS	1.62E-03	8.66E-04	4.44E-08	9.52E-08	5.70E-05	5.90E-04	8.03E-04	4.30E-04	7.74E-06	1.66E-05	5.92E-04	6.13E-03	1.16E-03	6.19E-04	3.18E-08	6.81E-08	8.67E-06	8.98E-05
MPW	2.14E-03	1.15E-03	5.89E-08	1.26E-07	7.56E-05	7.83E-04	1.05E-03	5.61E-04	1.01E-05	2.16E-05	7.72E-04	8.00E-03	6.36E-04	3.41E-04	1.75E-08	3.74E-08	4.77E-06	4.94E-05
	Cu						Zn						As					
TSS	3.76E-04	2.02E-04	1.03E-08	2.21E-08	1.22E-06	1.26E-05	5.57E-05	2.98E-05	1.53E-09	3.28E-09	4.68E-07	4.84E-06	1.40E-03	7.48E-04	3.83E-08	8.21E-08	2.93E-06	3.04E-05
TSW	4.07E-04	2.18E-04	1.12E-08	2.39E-08	1.32E-06	1.36E-05	5.90E-05	3.16E-05	1.62E-09	3.47E-09	4.96E-07	5.13E-06	1.35E-03	7.22E-04	3.70E-08	7.94E-08	2.83E-06	2.93E-05
SGS	2.57E-04	1.38E-04	7.07E-09	1.51E-08	8.33E-07	8.63E-06	6.27E-05	3.36E-05	1.72E-09	3.69E-09	5.27E-07	5.46E-06	1.22E-03	6.52E-04	3.34E-08	7.16E-08	2.55E-06	2.65E-05
SGW	2.12E-04	1.13E-04	5.81E-09	1.25E-08	6.85E-07	7.09E-06	1.80E-05	9.65E-06	4.95E-10	1.06E-09	1.51E-07	1.57E-06	2.14E-03	1.15E-03	5.89E-08	1.26E-07	4.50E-06	4.66E-05
SAW	2.88E-03	1.54E-03	7.90E-08	1.69E-07	9.31E-06	9.64E-05	1.78E-04	9.51E-05	4.88E-09	1.05E-08	1.49E-06	1.55E-05	2.87E-03	1.54E-03	7.90E-08	1.69E-07	6.04E-06	6.25E-05
MPS	9.91E-04	5.31E-04	2.72E-08	5.83E-08	3.21E-06	3.32E-05	1.38E-04	7.39E-05	3.79E-09	8.12E-09	1.16E-06	1.20E-05	4.01E-03	2.15E-03	1.10E-07	2.36E-07	8.42E-06	8.72E-05
MPW	5.72E-04	3.06E-04	1.57E-08	3.37E-08	1.85E-06	1.92E-05	2.95E-05	1.58E-05	8.11E-10	1.74E-09	2.48E-07	2.57E-06	3.76E-04	2.02E-04	1.03E-08	2.22E-08	7.90E-07	8.18E-06

	Se						Cd						Sb					
	Ingestion		**inhalation**		**dermal**		**Ingestion**		**inhalation**		**dermal**		**Ingestion**		**inhalation**		**dermal**	
	Children	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**	**Children**	**Adults**
TSS	5.92E-05	3.17E-05	1.63E-09	3.48E-09	-	-	3.73E-05	2.00E-05	1.80E-08	3.85E-08	7.82E-08	8.10E-07	3.84E-05	2.05E-05	1.05E-09	2.26E-09	-	-
TSW	3.88E-05	2.08E-05	1.07E-09	2.28E-09	-	-	2.63E-05	1.41E-05	1.27E-08	2.72E-08	5.52E-08	5.72E-07	5.75E-05	3.08E-05	1.58E-09	3.39E-09	-	-
SGS	1.53E-05	8.22E-06	4.21E-10	9.03E-10	-	-	2.41E-05	1.29E-05	1.16E-08	2.49E-08	5.06E-08	5.24E-07	5.21E-05	2.79E-05	1.43E-09	3.06E-09	-	-
SGW	2.15E-05	1.15E-05	5.90E-10	1.26E-09	-	-	1.10E-05	5.87E-06	5.28E-09	1.13E-08	2.30E-08	2.38E-07	5.48E-05	2.94E-05	1.51E-09	3.23E-09	-	-
SAW	5.79E-05	3.10E-05	1.59E-09	3.41E-09	-	-	2.82E-04	1.51E-04	1.36E-07	2.91E-07	5.91E-07	6.13E-06	7.95E-05	4.26E-05	2.18E-09	4.68E-09	-	-
MPS	3.36E-04	1.80E-04	9.24E-09	1.98E-08	-	-	1.03E-04	5.52E-05	4.96E-08	1.06E-07	2.16E-07	2.24E-06	1.01E-04	5.43E-05	2.78E-09	5.97E-09	-	-
MPW	2.50E-05	1.34E-05	6.86E-10	1.47E-09	-	-	1.97E-05	1.06E-05	9.51E-09	2.04E-08	4.14E-08	4.29E-07	2.74E-05	1.47E-05	7.53E-10	1.61E-09	-	-
	Ba						**Hg**						**Pb**					
TSS	6.73E-05	3.61E-05	1.85E-09	3.96E-09	-	-	8.37E-04	4.48E-04	8.02E-08	1.72E-07	1.76E-06	1.82E-05	7.38E-04	3.96E-05	2.03E-08	4.35E-08	1.03E-05	1.07E-04
TSW	7.95E-05	4.26E-05	2.18E-09	4.68E-09	-	-	2.41E-04	1.29E-04	2.31E-08	4.95E-08	5.06E-07	5.24E-06	9.26E-04	4.96E-05	2.55E-08	5.45E-08	1.30E-05	1.34E-04
SGS	5.78E-05	3.09E-05	1.59E-09	3.40E-09	-	-	4.31E-04	2.31E-04	4.13E-08	8.85E-08	9.05E-07	9.38E-06	1.90E-03	1.02E-04	5.23E-08	1.12E-07	2.67E-05	2.76E-04
SGW	1.09E-04	5.83E-05	2.99E-09	6.41E-09	-	-	3.65E-06	1.96E-06	3.50E-10	7.50E-10	7.67E-09	7.95E-08	4.65E-04	2.49E-05	1.28E-08	2.74E-08	6.51E-06	6.75E-05
SAW	2.65E-04	1.42E-04	7.29E-09	1.56E-08	-	-	3.65E-06	1.96E-06	3.50E-10	7.50E-10	7.67E-09	7.95E-08	2.66E-02	1.43E-03	7.31E-07	1.57E-06	3.73E-04	3.86E-03
MPS	2.49E-04	1.33E-04	6.83E-09	1.46E-08	-	-	1.83E-05	9.78E-06	1.75E-09	3.75E-09	3.84E-08	3.97E-07	2.96E-03	1.59E-04	8.13E-08	1.74E-07	4.14E-05	4.29E-04
MPW	9.88E-05	5.29E-05	2.71E-09	5.82E-09	-	-	3.65E-06	1.96E-06	3.50E-10	7.50E-10	7.67E-09	7.95E-08	9.28E-04	4.97E-05	2.55E-08	5.46E-08	1.30E-05	1.35E-04