

Geochemistry of Siloam and Tshipise Geothermal Springs, Limpopo Province, South Africa

¹Olatunde Samod Durowoju, ¹John Ogony Odiyo and ²Georges-Ivo Ekosse Ekosse

¹Department of Hydrology and Water Resources,

²Directorate of Research and Innovation,

University of Venda, Private Bag X5050, Thohoyandou 0950, South Africa

Article history

Received: 25-09-2017

Revised: 14-10-2017

Accepted: 30-03-2018

Corresponding Author:

Olatunde Samod Durowoju
Department of Hydrology and
Water Resources, University of
Venda, Private Bag X5050,
Thohoyandou 0950, South
Africa

Email: durotunde@gmail.com

Abstract: Geothermal springs are natural geological phenomena that occur throughout the world, and South Africa (SA) is endowed with several springs of this nature. Most of the geothermal springs in SA (31%) are found in Limpopo Province. Assessment of geochemistry of Siloam and Tshipise geothermal springs were undertaken during 2014 winter (May – July) and summer (October – December) seasons. Water samples were collected from the springs and stored at low temperatures (+/- 4°C) for analysis of hydrochemical parameters and acidification was carried out before trace metals analyses. The results show that Siloam and Tshipise geothermal springs water are not suitable for drinking due to high pH, high fluoride concentrations and some metals such as Hg, Ni and Pb. Various index methods such as Sodium Percentage (SP), Sodium Absorption Ration (SAR), Residual Sodium Carbonate (RSC), Permeability Index (PI), Kelly's index (KR) and Electrical Conductivity (EC) were used to evaluate groundwater quality for irrigation and most of the index has a similar result. Hence, the spring water is suitable for irrigation purposes. The water type is Na-Cl in both seasons for both site except for Siloam in winter having Na-HCO₃. There were slight variations in the hydrochemical compositions of geothermal spring water, although they were not significant ($p > 0.05$). However, there were significant differences in mean trace elements concentrations in geothermal spring water in summer compared to winter season ($p < 0.1$) for both Siloam and Tshipise springs. This can be attributed to the rainfall in summer which aids in more dissociation of rock particles and the release of more trace elements. Variations in mean trace elements concentrations could also be linked to the differences in fundamental changes in water chemistry from deep sources of the geothermal springs. It has thus been established and/or inferred that the dominant processes controlling the geothermal water are geothermal gradient, silicate weathering, mineral dissolution, cation exchange and inverse cation exchange.

Keywords: Geothermal Springs, Mineral/Rock Dissolution, Siloam, Tshipise, Variation, Water Chemistry

Introduction

Geothermal springs are natural geological phenomena that occur throughout the world (Lund, 2000). Ancient civilisations revered geothermal springs because they were believed to have supernatural and healing powers (La Moreaux and Tanner, 2001). Geothermal springs develop when surface water percolates into the earth and encounters hot volcanic masses of rock. The water is heated and returns along

faults, to the surface of the earth, like hot water. The same process occurs when rainwater penetrates the ground, infiltrates to great depths where it becomes heated, and then returns to the earth's surface while it is still hot (Higgins and Higgins, 1996).

People have used water from geothermal springs for different purposes for thousands of years (Olivier *et al.*, 2011). Documentary and oral history reveal that geothermal springs were used for bathing, medicinal, religious, hygienic and social purposes across the world,

for instance in India, Crete, Egypt, Turkey, Japan, Brazil and Canada (Lund, 2000; Van Vuuren, 1990). In addition to the increasing popularity of spas and the growing importance attached to the 'natural' health industry (Smith and Puczko, 2009), a real boom in popularity of the use of mineral water comes with the extensive hydrological exploration and undiscovered hydro-mineral resources. Promoting mineral spas and health resorts began in the 1950s and 1960s (Vassileva, 1996). Geothermal springs are increasingly being used for power generation, industrial processing, agriculture, aquaculture, bottled water and the extraction of rare elements (Lund, 2000; Vimmerstedt, 1998; Hellman and Ramsey, 2004; Petraccia *et al.*, 2005).

Limpopo Province in South Africa is richly-endowed with about twenty-four (24) known geothermal springs. Some of these have been developed for recreational and touristic purposes, while water from some of them is bottled and sold for therapeutic purposes (Olivier *et al.*, 2010). The chemistry of geothermal waters has attracted the attention of numerous studies, in particular, investigations of the influence of water-rock interactions and the vast diversity of the ionic composition of fluids that are found in geothermal systems. Some of such studies include those of (Mazor and Verhagen, 1983; Olivier *et al.*, 2010; 2011; Durowoju, 2015; Durowoju *et al.*, 2015).

The chemistry of water is very dynamic, mostly controlled and modified by its medium of contact. Since the chemical composition of water directly hints to the quality of water for various purposes, its monitoring and assessment gained substantial importance in the present century. A tremendous increase in the population increased the stress on both surface and groundwater. It was believed at the beginning of human civilisation itself, and groundwater was the most trusted form of drinking water because of the filtering effect of the aquifer. However, in the present world, drinking the water directly from the source without proper water quality monitoring and treatment is not recommended. Groundwater types have been used by many researchers in their studies to understand the controlling factors of the water chemistry (Aris *et al.*, 2009; Mondal *et al.*, 2010; Rajesh *et al.*, 2010; Ramesh and Elango, 2011).

The study of concentrations of various ions present in geothermal spring is used to describe the chemical characteristics of groundwater and in the identification of geochemical processes. The chemical composition of groundwater results from the hydrogeochemical processes occurring as the water reacts with the geological materials from which the water flows through (Aastri, 1994). Hydrochemical evaluation of groundwater systems is usually based on the availability of a significant amount of information concerning groundwater chemistry such as general geology, the

degree of chemical weathering of the various rock types, quality of recharge water and inputs from sources other than water-rock interaction (Aghazadeh and Mogaddam, 2004; Hossein, 2004; Subramani and Elango, 2005; Schiavo *et al.*, 2006; Aghazadeh and Mogaddam, 2010).

Siloam and Tshipise geothermal springs are located in the rural areas where the principal uses are mainly domestic and recreation. Recent studies on these sites have discussed the physical and chemical characteristics of these geothermal springs (Olivier *et al.*, 2010; Mazor and Verhagen, 1983; Olivier *et al.*, 2008) but none has shown the main factors and mechanism controlling the geothermal springs. Hence, this study integrates physical and geochemical data from the geothermal system to determine the primary factors and mechanism controlling the chemistry of the geothermal springs in the area. Also, this study assessed the seasonality of hydrochemical parameters of Siloam and Tshipise geothermal springs in winter and summer seasons; explore various index methods to ascertain their suitability for irrigation and the thermal property of the geothermal springs in comparison with previous studies in the research areas.

Materials and Methods

Study Area

Tshipise and Siloam geothermal springs are located in the Limpopo Province of South Africa (Fig. 1) and are of different surface geology but fall on the Soutpansberg Group (Durowoju, 2015). The study areas are characterised with high temperature variations at various seasons of the year with temperature in winter ranging from 16°C to 22°C and summer ranging from 22°C to 40°C (Makungo *et al.*, 2010). The mean annual rainfall of Nzhelele ranges from 350-400 mm per annum (Makungo *et al.*, 2010). The Siloam spring is found in Nzhelele Valley at Siloam Village which falls under the youngest Formation of the Soutpansberg Group, which is the Sibasa Formation. It is dominated by basalt (Fig. 2), which originated from the lava at the base of the Formation. Siloam geothermal spring is located on the coordinate of 22° 36' 05.48" S and 30° 10' 23.01" E. Tshipise spring is found further north of the leeward side of the Soutpansberg Mountain Range. The spring is underlain by volcanic rocks of the Letaba Formation at Karoo Super Group. Tshipise geothermal spring is on 22° 53' 09.66" S and 30° 12' 40.36" E of the equator. The Letaba Formation immediately underlying the spring at Tshipise comprises mainly of basalt, arenite and marble (Fig. 2). Further details of the study areas and the geology are described in Durowoju (2015; Durowoju *et al.*, 2016).

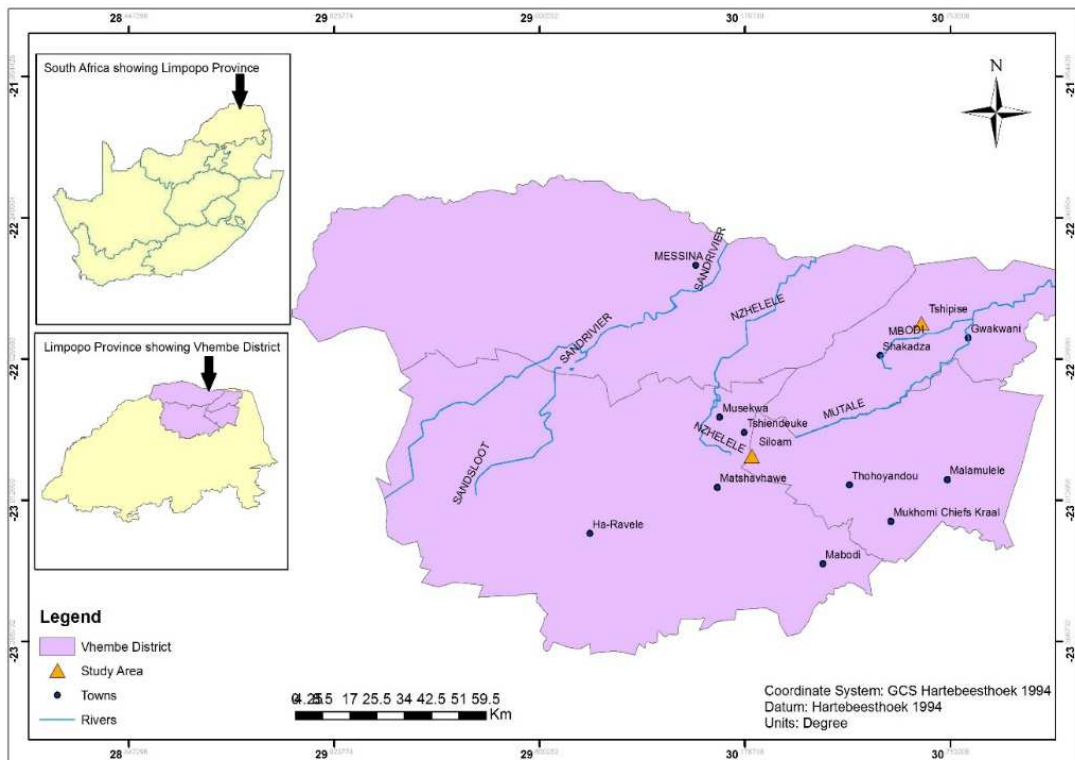


Fig. 1: Map of Vhembe District showing Siloam and Tshipise geothermal springs, Limpopo Province, South Africa

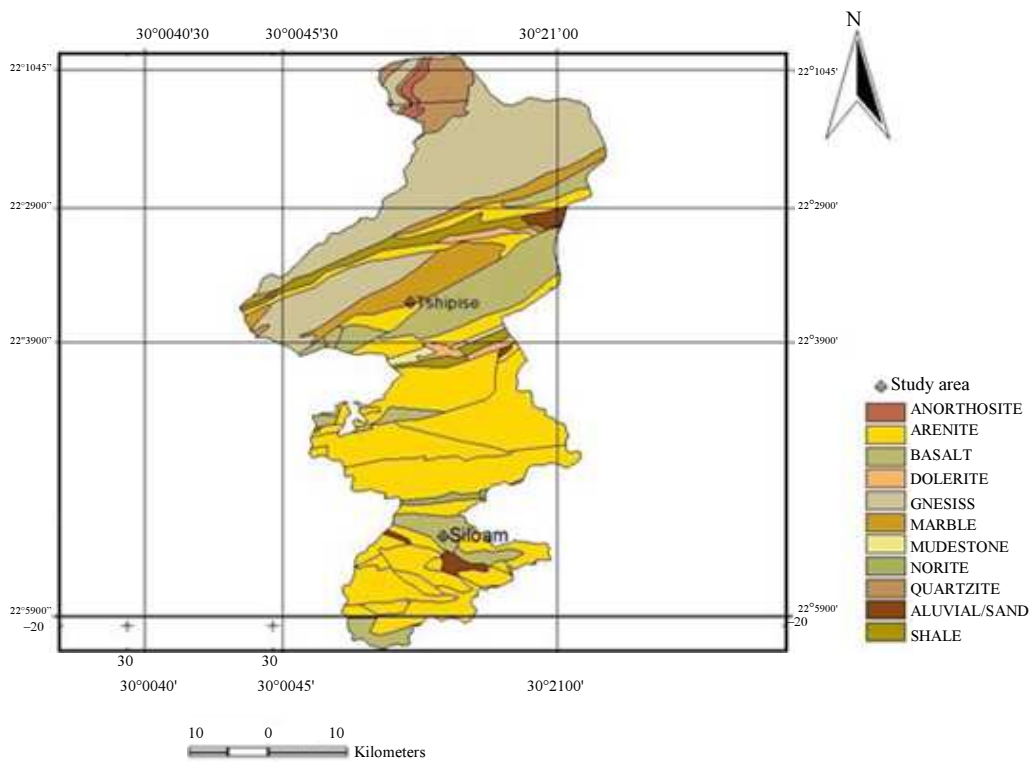


Fig. 2: Geological map of Siloam and Tshipise areas

Sampling and Analyses

Water samples were collected at Siloam and Tshipise geothermal springs during winter and summer seasons from May – December 2014. Water samples were collected thrice per season to obtain seasonality (Yahaya *et al.*, 2009). The geothermal water samples were collected at the source using acid-washed high-density polyethylene (HDPE) containers, chilled to between 3 to 5°C (USEPA, 2004) and dispatched in a cooler box to Agricultural Research Council (ARC-ISCW) laboratory, Pretoria. The samples were allowed to cool before pre-treatment due to the high temperature of water. The HDPE containers were rinsed properly with spring water to avoid cross-contamination. Water temperatures together with other physical parameters such as pH, Electrical Conductivity (EC) and Total Dissolved Solids (TDS) were measured in the field using portable, multi-sensor meter (Multi 340i/SET, USA) as suggested by the American Public Health Association (APHA, 1998). Samples were analysed for hydrochemical parameters in the laboratory using the standard recommended methods (APHA, 1998). The sample pH, Sodium Absorption Ratio (SAR), alkalinity and temporary hardness were determined using ManTech Titrasip Autotitrator. The samples for anions (F⁻, Cl⁻, NO₃⁻, SO₄²⁻, PO₄³⁻, HCO₃⁻) were filtered and analysed by using the Ion chromatography method (Dionex Model DX 500). Samples for major cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) and trace metals were filtered and acidified with concentrated nitric acid (2 ml/litre); analysed using ICP-MS analytical method (Agilent 7700 series).

Quality assurance/Quality control (QA/QC) was incorporated into geothermal spring water sampling and analyses to enhance sample integrity, increase the confidence of analytical data as reliable analytical information, and to prevent reporting wrong positive values caused by contamination. Field blank and splits were ensured for the water samples. The instruments used were calibrated with a standard solution to avoid analytical errors. The method detection limit (MDL) for each cation was obtained by US EPA method 200.8 (USEPA, 1994). The MDL for each cation is 0.03 µg/L (Na⁺), 0.07 µg/L (Mg²⁺), 0.4 µg/L (K⁺) and 0.03 µg/L (Ca²⁺). MDL for each anion were determined according to US EPA method 300.0, rev 2.1 (USEPA, 1993) accuracy measurements methodology. MDLs for each anion are 25 µg/L (F⁻), 12.5 µg/L (NO₃⁻), 500 µg/L (Cl⁻), 125 µg/L (SO₄²⁻) and 150 µg/L (PO₄³⁻). The samples were analysed in triplicate to obtain the mean values of the concentrations.

The piper diagram, Gibbs plot, plot of (Ca+Mg) vs (HCO₃+SO₄) and the pie chart were plotted using Groundwater Chart and Microsoft Excel (2013), to explain water chemistry, distribution and the variations in the hydrochemical composition of the geothermal spring's water with respect to seasons. Chloro-Alkaline

Indices [CAI-1 and CAI-2] were calculated (expressed as meq/l) using equations 1 and 2 to find out the ion exchange processes responsible for the concentration of ions in groundwater (Aghazadeh and Mogaddam, 2010):

$$CAI-1 = [Cl^- - (Na^+ + K^+)] / Cl^- \quad (1)$$

$$CAI-2 = [Cl^- - (Na^+ + K^+)] / (SO_4^{2-} + HCO_3^- + CO_3^- + NO_3^-) \quad (2)$$

Residual Sodium Carbonate (RSC) has been calculated to determine the hazardous effect of carbonate and bicarbonate on the quality of water for agricultural purpose using Equation (3):

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \quad (3)$$

where, all ionic concentrations are expressed in meq/l (USEPA, 1993).

The Permeability Index (PI) values also indicate that the groundwater is suitable for irrigation and it is defined as follows (Equation 4):

$$PI = 100 * ([Na^+] + \sqrt{[HCO_3^-]}) / ([Na^+] + [Ca^{2+}] + [Mg^{2+}]) \quad (4)$$

where, all the ions are expressed in meq/l (Domenico and Schawartz, 1990).

Kelly (1946) and Wilcox (1958) were also deployed to determine the hazardous effect of sodium on water quality for irrigation usage in terms of Kelly's Ratio (KR) and sodium percentage (SP), respectively. Kelly's ratio and SP are computed as:

$$KR = Na^+ / (Ca^{2+} + Mg^{2+}) \quad (5)$$

$$SP = 100 * (Na^+ + K^+) / (Ca^{2+} + Mg^{2+} + Na^+ + K^+) \quad (6)$$

All ionic concentrations are in meq/l

Results and Discussion

Thermal Properties of the Spring

The temperatures obtained from studied geothermal springs were compared with published values (Olivier *et al.*, 2010; 2008; Kent, 1949) to ascertain any thermal variations with respect to time. The thermal properties of geothermal springs show slight variations with the season (Fig. 3). Previous work by Kent (1949) and

Olivier *et al.* (2010; 2008) also reported slight changes in the thermal properties of these springs, which could not be accounted for. Siloam recorded 67.5°C in 2004, 62°C in 2010, 67.7°C in winter season (2014), 68.6°C in summer season (2014) while Tshipise recorded 57.2°C in 1949, 58°C in 2004/2010, 54.6°C in winter season (2014), and 55.7°C in summer season (2014). These changes can be attributed to seasonal variation which causes fluctuation in thermal property of the springs. During summer season, there is high rainfall and more groundwater (coupled with high flow rate), which is heated as a result of the geothermal gradient of 2°C - 3°C per 100 m (Press and Siever, 1986). This results in high temperature in summer compared to winter season. In both sites, there is approximately 1°C difference in the thermal property of the geothermal spring in summer season compared to winter season.

High water temperature in geothermal spring aids in more mineralisation of the water compared to non-geothermal spring water (Odiyo and Makungo, 2012). Thermal properties of these geothermal springs have shown slight variations over ten years and more (Fig. 3). In each study site, the temperature obtained during summer season was not significantly different from the temperature obtained during winter season (Fig. 3). This implies that the geothermal gradient of the springs is the major controlling factor.

Chemical Composition

Groundwater naturally contains several different dissolved inorganic constituents which make up its composition and propose its usability. Groundwater in this study has been sampled in two different geothermal springs, and the results of the chemical analyses are

shown in Tables 1 and 2. The measured pH values are 9.43 and 9.57 at Siloam, 8.91 and 8.93 at Tshipise for winter and summer seasons, respectively. The pH values obtained at Siloam exceeded the recommended South African Guidelines for Domestic Water Quality (SABS, 1999) values of 6-9. There is a strong negative correlation between pH and alkalinity; high pH value results in low alkalinity value (Makwe and Chup, 2013). This accounts for higher alkalinity in winter season than summer season for both geothermal springs. The SAR values for Siloam and Tshipise were >1. This makes geothermal water not to be suitable for drinking but suitable for irrigation. Since, the SAR value range from 6.9-14.55 which falls within good and excellent irrigation groundwater quality (Raghunath, 1987). TDS values were 188.4 mg/L and 214 mg/L at Siloam; 428.4 mg/L and 467.49 mg/L at Tshipise for winter and summer, respectively. The TDS and EC values at Tshipise in summer season (467.49 mg/L and 800 µS/cm) exceeded the values for Domestic Water Quality of 450 mg/L and less than 800 µS/cm, respectively (SABS, 1999). This could possibly be as a result of the high temperature contributing to increased mineral dissolution from rainfall in summer at Tshipise. Generally, higher TDS and EC at Tshipise than Siloam is an indication of more mineral availability at Tshipise than Siloam. The EC values fall within the medium salinity class which implies that the water is good for irrigation purposes. According to the classification, the geothermal water was not suitable for irrigation. From the Wilcox diagram, the geothermal water can be classified into C1; C2 and S1; S2 (Fig. 4), which implies that the water has low/medium alkalinity and salinity hazard which is suitable for irrigation.

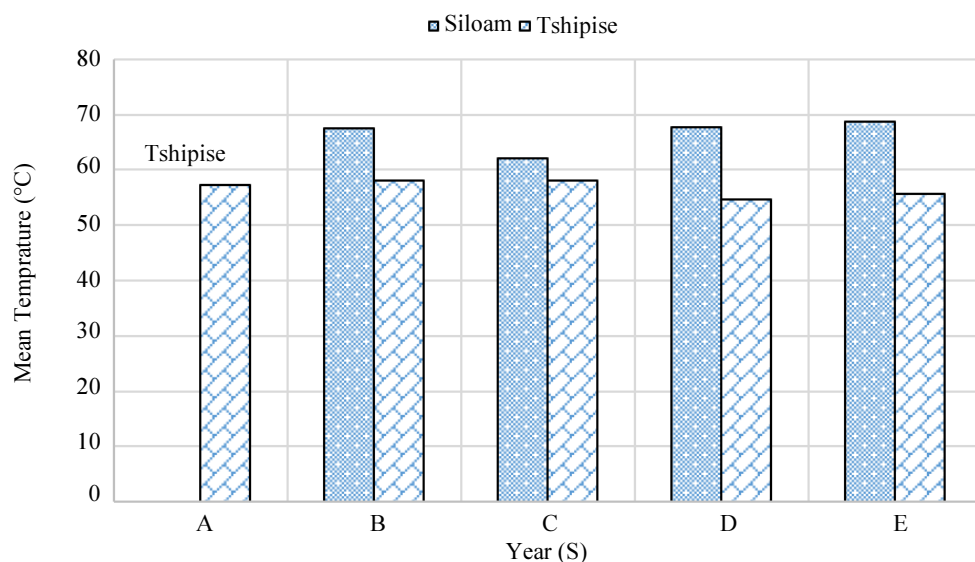


Fig. 3: Trends of temperature variations from studies by Kent (1949); Olivier *et al.* (2008; 2010); **Note:** A – 1949, B – 2004, C – 2010, D – Winter 2014 and E – Summer 2014

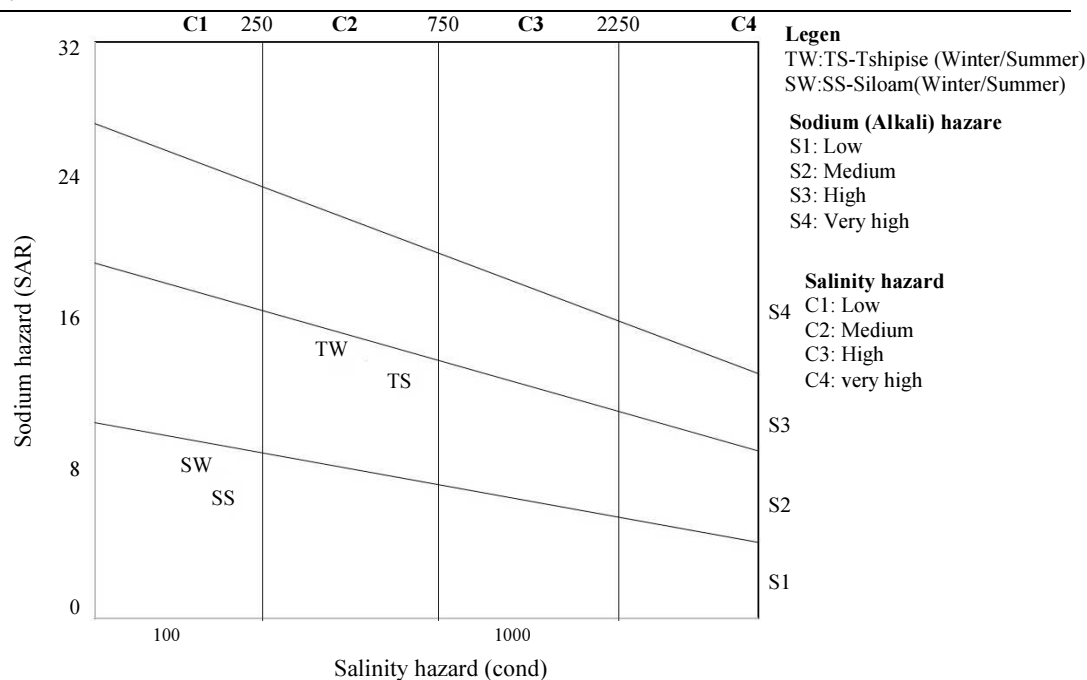


Fig. 4: Wilcox (US salinity) diagram for geothermal spring water sample for winter and summer seasons from the study area

Table 1: Mean values of the major and minor chemistry constituents data

	SABS, 1999	Tshipise W	Tshipise S	Siloam W	Siloam S
Temp. (°C)		54.6±2.26	55.7±4.24	67.7±3.68	68.9±4.24
pH	6 ≤ pH ≤ 9	8.91±0.27	8.93±0.04	9.43±0.18	9.57±0.24
pHs (pHs-pH±1)		8.34±0.20	8.6±0.07	8.64±0.06	8.7±0.07
SAR	1*	14.55±0.14	13.6±0.14	7.4±0.06	6.9±0.04
Elect. Conduct. (µS/cm)	<800	675±7.07	800±70.71	335±21.21	390±28.28
TDS (mg/L)	450	428.4±2.97	467.49±3.55	188.4±2.26	214±5.66
Alkalinity (mg/L)		157±4.24	111.5±4.95	106±4.24	104.5±2.12
Temp. Hard.(mg/L)		28±2.83	31.81±1.43	19.37±0.89	23.08±0.59
Anions and Cations (mg/L)					
Sodium	200	167.7±1.13	165.91±0.13	73.44±2.21	73.46±2.04
Potassium	50	4.2±0.28	4.18±0.11	2.65±0.07	2.56±0.06
Calcium		8.12±0.17	7.16±0.08	5.65±0.21	5.17±0.07
Magnesium		1.18±0.11	2.57±0.24	1.09±0.01	2.3±0.14
Fluoride	1.5;1*	6.72±0.31	7.28±0.25	6.66±0.23	5.97±0.24
Nitrate	6*	1.96±0.23	0.78±0.25	0.57±0.10	0.24±0.06
Chloride	200	97.04±2.88	161.17±4.00	24.65±1.63	48.01±0.16
Sulphate	400	44.46±0.65	56.85±2.62	9.03±0.18	13.09±0.41
Phosphate		2.31±0.27	0.33±0.04	0.84±0.06	0.00±0.00
Carbonate		7.05±0.21	5.7±0.28	15.75±0.35	16.5±0.57
Bicarbonate		177.21±3.13	111.02±1.44	97.3±3.25	93.94±1.50
RSC (meq/L)		3.49	2.14	2.12	2.06
PI (%)		102.3	100.5	103.9	102.7
% Na		94.87	94.59	91.86	91.05
KR		18.03	17.05	10.90	9.83
CAI-1 (meq/L)		-0.77	-0.06	-2.09	-0.58
CAI-2 (meq/L)		-0.33	-0.05	-0.42	-0.23

*DWAF (1996) value, (SABS) South African Bureau of Standards

Generally, the mean values of the temperature, pH, EC, TDS and temporary hardness were higher in summer compared to the winter season. This could be attributed to weathering intensity due to the increased

temperature gradient and increased amount of groundwater recharge (rainfall) (Makungo *et al.*, 2010). Fig. 5 evaluates the water types using Piper trilinear plot (Piper, 1944; Sajil Kamar, 2013). In general, piper diagram

is classified into 6 fields. They are 1. Ca-HCO₃ type 2. Na-Cl type 3. Ca-Mg-Cl type, 4. Ca-Na-HCO₃ type 5. Ca-Cl type 6. Na-HCO₃ type. In this study, Na-Cl is dominated water type found except for Siloam at winter having Na-HCO₃. Na-Cl water type is dominated by Na⁺ and Cl⁻, derived from Na-Cl brines in winter and summer seasons linked to the underlying geology. Na-Cl and Na-HCO₃ water types' showed a typical marine and deeper ancient groundwater influenced by ion exchange. There is no variation in the water type with season except for Siloam at winter. The Na⁺ and HCO₃⁻ 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⁺ increases from groundwater in the area due to water-rock interaction due to oxidizing condition and evapotranspiration processes. These findings support the previous studies by Olivier *et al.* (2011) as the water also falls under class C (temporary hard carbonate water) (Bond, 1946).

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, most of the water samples fall under marginal quality except for Tshipise water in winter, which is practically not suitable for irrigation. World Health Organisation (WHO) (WHO, 1989) uses a criterion for assessing the suitability of water for irrigation based on Permeability Index (PI). PI is classified under class I (>75%), class II (25-75%) and class III (<75%) orders, with class I and II good for irrigation. According to the PI values, the geothermal water can be designated as class I (above 75%) and this implies that the water is excellent for irrigation (Doneen, 1964; Aastri, 1994). Since there is little or no difference in the PI per season for both sites, this implies that the groundwater has no permeability and infiltration problems. The concentration of Na⁺ measured against Ca²⁺ and Mg²⁺ is known as Kelly's Ratio (KR), based on which irrigation water can be rated (Kelly, 1946). Kelly's ratio of water is categorized into suitable if KR is <1, marginal when KR is 1-2 and unsuitable if KR is >2 (Kelly, 1946). According to the classification, the geothermal water was not suitable for irrigation. This corroborates with the Sodium Percentage (SP), which is above 50% for both seasons in study sites resulting to non-suitability of the water for irrigation.

The mechanism to which, Na⁺, Ca²⁺ and other components are added to groundwater may be assessed by plotting the water chemistry data into Gibbs diagram (Gibbs, 1970). The diagram defines three geochemical processes controlling groundwater chemistry. Siloam and Tshipise geothermal springs data fall in the water-rock interaction field (Fig. 6). Thus, Gibbs plot indicates

that geothermal spring water chemistry is controlled mainly by water-rock interaction process leading to 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).

The chloro-alkaline indices CAI 1, 2 indicate the ion exchange 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 1 and 2. The direct exchange occurred when the indices are positive, meaning that there is ion exchange of Na and K from the water with Mg²⁺ and Ca²⁺ in the rock and vice versa. The CAI 1, 2 calculated from the waters of the study area gave negative values (Table 1) and this implies the presence of base-exchange reaction. Ca²⁺ and Mg²⁺ exchange Na⁺ sorbed on the exchangeable sites on the aquifer minerals, resulting in the decrease of Ca and Mg and increase of Na⁺ in the groundwater by reverse ion exchange (Schoeller, 1977; Glover *et al.*, 2012). This confirms that Ca²⁺, Mg²⁺ and Na⁺ concentrations are interrelated through reverse ion exchange.

Datta and Tyagi (1996) and Lakshmanan *et al.* (2003) revealed that plot (Ca + Mg) v (HCO₃+SO₄) is also another tool to determine the geochemical processes. Plot (Ca + Mg) v (HCO₃+SO₄) shows the distribution of geothermal water between silicate and carbonate weathering processes (Fig. 7). The plot distinguishes between carbonate and silicate weathering controlling factors. The water samples fall below the 1:1 line, which implies that they are in the field of silicate weathering (Fig. 7). This corroborates the above evidence that the weathering processes are dominant.

Table 2 shows the mean values for trace element concentrations in the geothermal springs, which implies that geothermal water is highly mineralised owing to the geological composition as supported by Todd (1980). Table 2 also compares the present findings with the standard guidelines for drinking water by SABS (1999) and WHO (2000). According to the South African drinking water standards, the geothermal water contains unacceptably high values of Ni (868 µg/L; 462.11 µg/L) and Pb (652 µg/L; 211 µg/L) during summer at Tshipise and Siloam, respectively, and high value of Hg in Tshipise during summer (Table 2). This could possibly be as a result of higher temperature and rainfall in summer resulting in more mineralisation. This is worrisome particularly on the health impacts of the inhabitants. Elemental lead, mercury and nickel are very toxic leading to high blood pressure and kidney damage; affecting the central and peripheral nervous systems leading to brain damage; lung fibrosis, cardiovascular and kidney diseases, respectively.

Table 2: Mean trace elements concentrations in the geothermal springs

Elements	WHO; SABS μg/l	Tshipise S μg/l	Tshipise W μg/l	Siloam S μg/l	Siloam W μg/l
Li		58.97	51.15	13.74	10.01
Be		0.05	0.04	0.04	0.04
B		31.23	18.27	4.83	0.03
Ti		1.23	2.25	3.27	3.99
V		0.15	0.03	3.2	2.63
Cr	50; 100	0.41	0.06	0.03	0.06
Mn	500; 100	7.2	0.63	1.34	0.19
Co		9.65	0.01	0.18	0.01
Ni	20; 150	868	0.05	462.11	0.63
Cu	2000; 1000	45.39	0.51	0.13	0.24
Zn	3000; 5000	348	0.17	342	0.12
As	10; 10	0.41	0.06	0.33	0.11
Se	10; 20	3	1.07	0.1	0.55
Rb		11.34	14.77	13.29	16.66
Sr		213.5	211.33	8.73	11.33
Mo		1.58	1.14	1.64	1.1
Cd		23.19	0.2	0.24	0.02
Sn		2.09	0.09	2.23	0.09
Sb	5; 5	0.71	0.01	0.02	0.01
Te		0.13	0.03	0	0.09
Cs		13.69	1.26	0.47	0.54
Ba		18.78	17.05	6.68	9.15
La		0.12	0.02	0.01	0.02
W		4.42	2.73	0.87	1.27
Pt		0.1	0.01	0.02	0.01
Hg	1; 1	1.78	0.25	0.64	0.04
Tl		0.42	0.04	0.01	0.04
Pb	10; 20	652	0.05	211	0.01
Bi		0.1	0.01	0.03	0.01
U		0.05	0.01	0.01	0.01

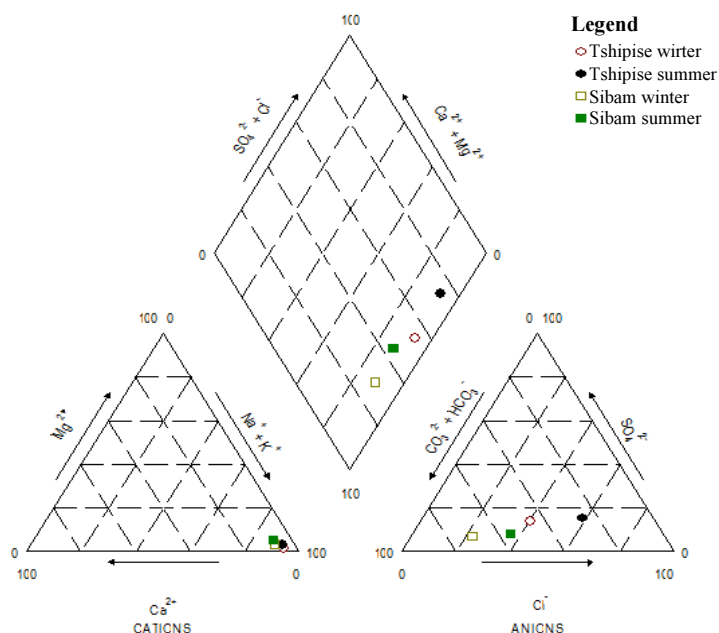


Fig. 5: Piper trilinear diagram showing the water type in the studied geothermal springs

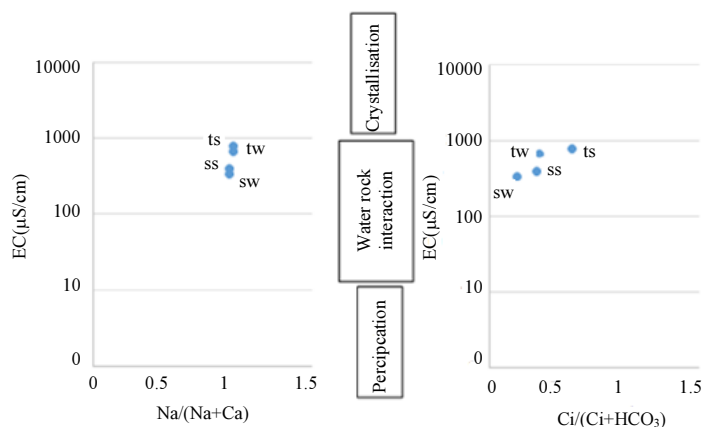


Fig. 6: Gibbs plot for Siloam and Tshipise geothermal springs; Note: ss - Siloam summer, sw – Siloam winter, ts – Tshipise summer, tw – Tshipise winter

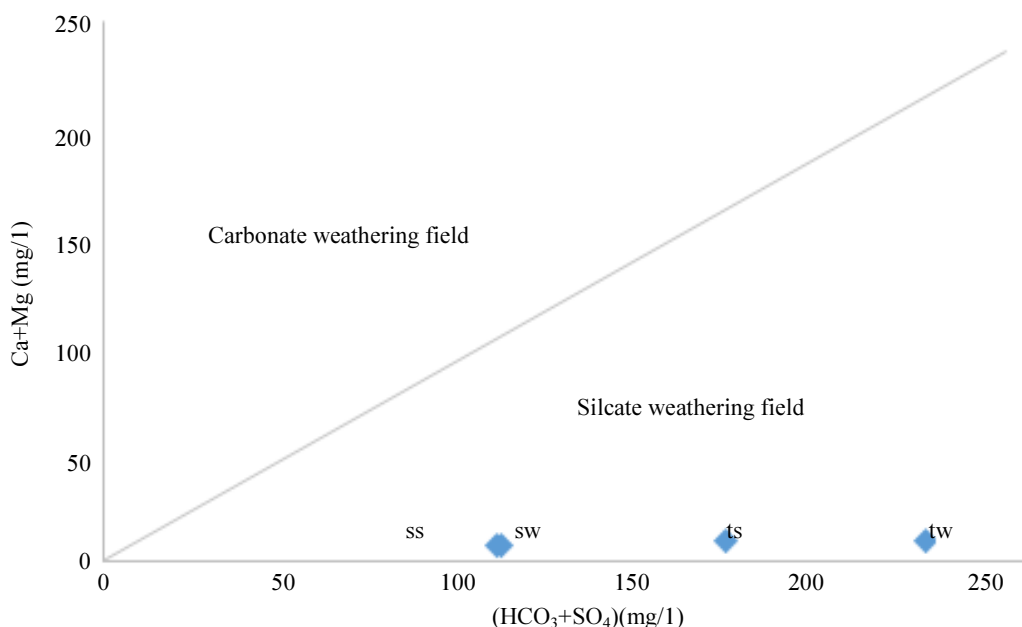


Fig. 7: Plot (Ca+Mg) vs (HCO₃+SO₄) for Siloam and Tshipise geothermal springs

Comparison with previous study by Olivier *et al.* (2011) shows that there are differences in the concentrations of the trace elements, though the magnitude of the differences may not necessarily be much. This implies that there are reasonable differences in the trace element concentrations of the springs over the last four years. These could be as a result of the anthropogenic factors. At each study site, there are significant differences in the trace elements concentrations in different seasons (ANOVA, $p < 0.1$) but no significant differences at $p < 0.05$ ($0.05 < p < 0.1$). Tshipise geothermal spring water was found to be more mineralized than Siloam spring water and this could be as a result of the high TDS, EC and undying

geology of the spring.

Figure 8 shows clearly that the trace elements concentrations follow the same trend but vary in magnitude of concentrations. Also, there are more trace elements in summer compared to the winter season. This can be attributed to rainfall in summer. Rainfall aids in more dissociation of rock particles (underlying geology) and the release of abundant trace elements as explained earlier. Elements like Li, Be, B, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sn, Sb, Te, Cs, Ba, La, W, Pt, Hg, Tl, Pb, Bi and U are higher in concentrations in summer than in winter season at least in one of the two springs. Nevertheless, elements like Ti and Rb are higher in winter compared to summer.

This might be as a result of their insolubility/reactivity with water (exothermic reaction).

At Siloam, there are significant variations in trace element concentrations between winter and summer seasons (Fig. 9). Also, there are more trace elements in summer than winter, similar to the case of Tshipise spring. Elements like Li, B, V, Mn, Co, Ni, Zn, As, Mo, Cd, Sn, Sb, Pt, Hg, Pb and Bi, are higher in concentrations in summer compared to winter. However, Be, Ti, Cr, Cu, Se, Rb, Sr, Te, Cs, Ba, La, W and Tl are higher in concentrations in winter compared to summer, while U remains constant in both seasons. Rb is denser than water and so sinks easily. Rb has a strong correlation with Be, Cs, Ba, La, Tl, Te, Cr, Cu, Se, Sr and Ti. This accounts for their higher concentrations in the winter compared to the summer season.

Variations in Chemical Composition of the Geothermal Spring Water

The dominant ionic compositions found in Siloam and Tshipise spring waters are Sodium (Na^+), bicarbonate (HCO_3^-), sulphate (SO_4^{2-}) and chloride (Cl^-) (Table 1). The high Na^+ concentrations probably originate from sodium-rich plagioclase feldspars in the sandstone and shale. The general order of dominant cations is $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$; having 33%, 2%, 1% and 0% for winter and 32%, 1%, 1% and 1% for summer in Tshipise, respectively (Fig. 10). The sequence of the abundance of the anions is in the order: $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{F}^- > \text{NO}_3^- > \text{PO}_4^{3-}$. The percentages of

HCO_3^- , Cl^- and SO_4^{2-} are 35, 19 and 9 in winter and 22, 31, 11 in summer at Tshipise spring (Fig. 10). The relatively low bicarbonate concentration recorded at Tshipise can be attributed to the circulation of groundwater in lithologies with low carbonate composition, hence the silicate weathering (Fig. 7). Siloam geothermal spring followed almost the same trend as Tshipise geothermal spring in this order: $\text{HCO}_3^- > \text{Cl}^- > \text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{F}^- > \text{PO}_4^{3-} > \text{NO}_3^-$, although it had higher concentration of CO_3^{2-} than Tshipise (Fig. 11). Generally, high levels of fluoride in geothermal spring waters in these study areas are alarming and preventive measures are required to mitigate the effects. This is attributed to the fluoride forming minerals present in the geology of the springs.

In both sites, HCO_3^- concentrations decreased from winter to summer while Cl^- and SO_4^{2-} concentrations increased from winter to summer (Fig. 10 and 11). The decrease in the HCO_3^- concentration from winter to summer, could be as a result of more rainfall in summer, which aids more dissolution to release CO_2 to the atmosphere. The increase in the concentrations of Cl^- and SO_4^{2-} from winter to summer could also be due to more dissolution in rainwater. Generally, there were variations in the composition of the water from both geothermal springs, though not statistically significant. This implies that the source of the geothermal spring water was deep and therefore not only affected by seasonal rainfall recharge.

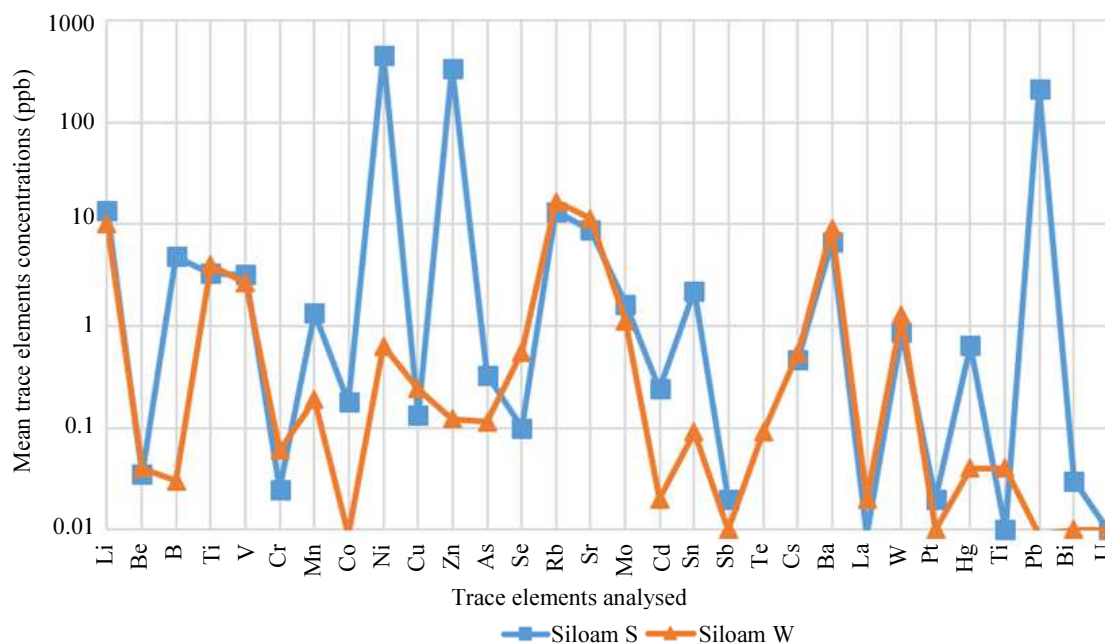


Fig. 9: Variation of the trace elements concentrations in Siloam Spring

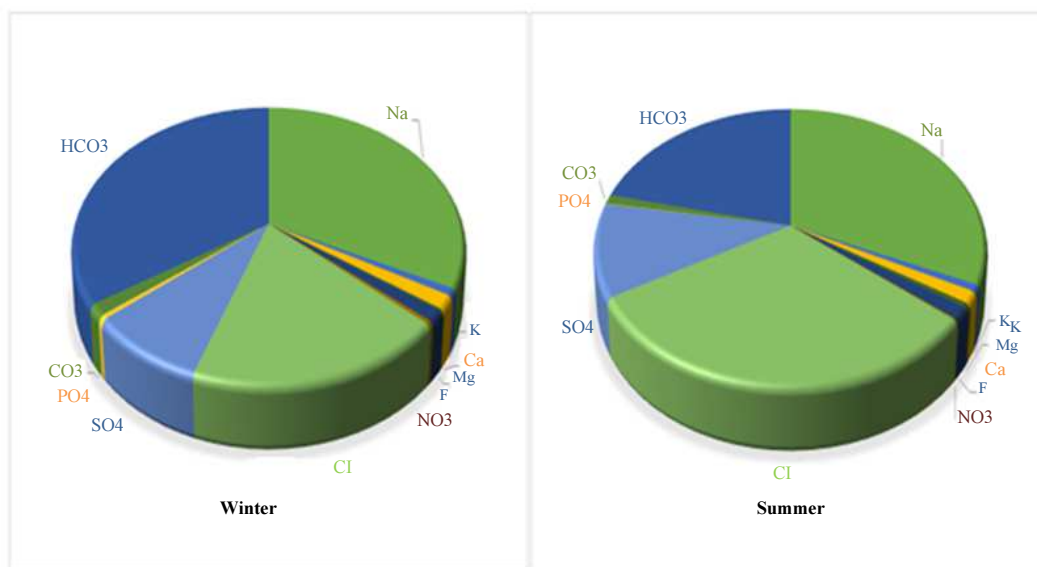


Fig. 10: Concentrations of the major ion species in Tshipise geothermal spring expressed as percentage of the total mineral composition in winter and summer seasons, respectively

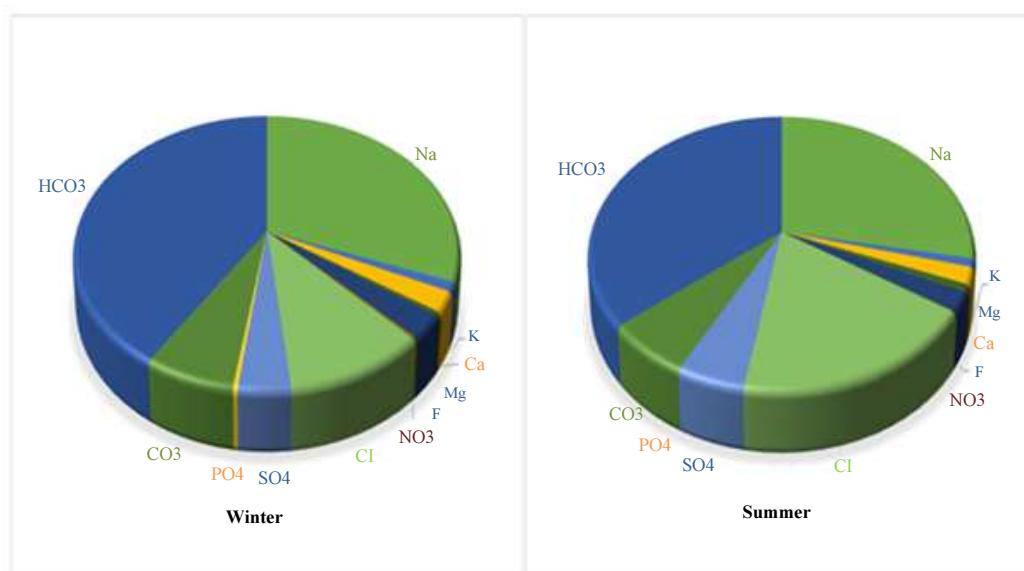


Fig. 11: Concentrations of the major ion species in Siloam geothermal spring expressed as percentage of the total mineral composition in winter and summer seasons, respectively

Conclusion

The chemical compositions of the geothermal springs waters have been shown to be above the compliance standard for drinking and irrigation in terms of F^- and SAR, respectively, in both springs; high pH-value at Siloam and high TDS value at Tshipise have also been shown. High fluoride concentration and high pH value make geothermal spring water unfit for drinking. The geothermal spring water from both springs is not suitable for irrigation, owing to its high SAR value, RSC and PI -

values. Various index methods such as SP, SAR, RSC, PI, KR and EC were used to evaluate groundwater quality for irrigation. Majority of index results were similar to SAR, RSC, PI, and EC except for KR and SP implying that the geothermal water samples fall under excellent to good category in winter and summer seasons. Because the geothermal spring water is used for drinking and other vast applications, they may have adverse environmental and health impacts on inhabitants and tourists that are exposed to contaminants through balneological applications. Results of the

hydrochemistry suggest that all the water samples are alkaline. Major processes controlling the geothermal water are the geothermal gradient, silicate weathering, mineral dissolution, cation exchange and inverse cation exchange processes. Assessment of hydrochemical parameters of geothermal springs showed that Siloam spring had Na-Cl water type in both seasons. Tshipise geothermal spring was found to have Na-HCO₃ in winter and Ca-Na-HCO₃ in summer. There were slight variations in the hydrochemical compositions of geothermal spring water, although it was not statistically significant ($p > 0.05$). However, there were significant differences in trace elements concentrations in geothermal spring water in summer compared to winter season ($p < 0.1$) for both Siloam and Tshipise springs. This shows that the sources of the geothermal springs were deep and could not only be affected by seasonal rainfall recharge. More rainfall in summer season enhances more rock-water interactions at the deep aquifer of the geothermal spring and more trace elements are released to the water body at the surface. This contributes to more trace elements in the geothermal water during summer than in the winter season.

Acknowledgments

The authors would like to thank National Research Foundation, Pretoria, South Africa and University of Venda for funding and various forms of support. Also, we thank Agricultural Research Council (ARC-ISCW) laboratory, Pretoria for the chemical analyses.

Author's Contributions

This section should state the contributions made by each author in the preparation, development and publication of this manuscript.

Conflicts of Interest

The authors declare no conflict of interest

References

- Aastri, J.C., 1994. Groundwater chemical quality in river basins, hydrogeochemical facies and hydrogeochemical modelling. PhD thesis Bharathidasan University, Tiruchirapalli, Tamil Nadu, India.
- Aghazadeh, N. and A.A Mogaddam, 2004. Evaluation of the effect of geological formation on groundwater quality in the Harzandat plain aquifer. Symposium Geosci. Iran, 22: 392-395.
- Aghazadeh, N. and A.A Mogaddam, 2010. Assessment of groundwater quality and its suitability for drinking and agricultural uses in the Oshnavieh area, Northwest of Iran. J. Environ. Protect, 1: 30-40.

- APHA, 1998. Standard Methods for the Examination of Water and Wastewater. 20th Edn., American Public Health Association, Washington DC, USA.
- Aris, A.Z., M.H Abdullah and K.W Kim, 2009. Praveena SM, Hydrochemical changes in a small tropical island's aquifer: Manukan Island, Sabah, Malaysia. Environ Geol., 56: 1721-1732.
- Bond, G.W., 1946. A geochemical survey of the underground water supplies of the Union of South Africa. Memoirs Geol. Surv. S. Afr., 41: 208-208.
- Datta, P.S. and S.K. Tyagi, 1996. Major ion chemistry of groundwater in Delhi area: Chemical weathering processes and groundwater flow regime. J. Geol. Society India, 47: 179-188.
- DWAF, 1996. South African water quality guidelines. Domestic Water Use.
- Domenico, P.A. and F.W. Schwartz, 1990. Physical and Chemical Hydrogeology. 1st Edn., John Wiley and Sons, New York.
- Doneen, L.D., 1964. Notes on Water Quality in Agriculture. 1st Edn., Department of Water Science and Engineering, University of California, Davis. pp: 96.
- Durowoju, O., J. Odiyo and G. Ekosse, 2015. Hydrogeochemical setting of geothermal springs in Limpopo Province, South Africa. Res. J. Chem. Environ., 19: 77-88.
- Durowoju, O., J. Odiyo and G. Ekosse, 2016. Variations of heavy metals from geothermal spring to surrounding soil and Mangifera indica-Siloam Village, Limpopo Province. Sustainability, 8, 60-0. DOI: 10.3390/su8010060
- Durowoju, O.S., 2015. Trace element concentrations in geothermal springs and their impact on soil and vegetation in Siloam and Tshipise, Master's dissertation. University of Venda, South Africa.
- Eaton, F.M., 1950. Significance of carbonate in irrigation water. Soil Sci., 69: 123-133.
- Gibbs, R.J., 1970. Mechanisms controlling world water chemistry. Science, 170: 1088-1090
- Glover, E.T., T.T. Akiti and S. Osaе, 2012. Major ion chemistry and identification of hydrogeochemical processes of groundwater in Accra Plains. Elixir Geoscience, 50: 10279-10288.
- Hellman, M.J. and M.S. Ramsey, 2004. Analysis of hot springs and associated deposits in Yellowstone national park using ASTER and AVIRIS remote sensing. J. Volcanol. Geothermal Res., 135: 195-219.
- Kelly, W.P., 1946. Permissible composition and concentration of irrigation waters. Proc. ASC.
- Higgins, M.D. and R.A Higgins, 1996. Geological Companion to Greece and the Aegean. 1st Edn., Gerald Duckworth, London, United Kingdom.
- Hossein, M.T., 2004. Hydrochemical evaluation of groundwater in the Blue Nile Basin, eastern Sudan, using conventional and multivariate techniques. Hydrogeol. J., 12: 144-158.

- Kent, L.E., 1949. Thermal waters of the Union of South Africa and South West Africa. *Trans. Geol. Soc. WS. Afr.*, 52: 231-264.
- La Moreaux, P.E. and J.T Tanner, 2001. *Springs and Bottled Waters of the World: Ancient History, Source, Occurrence, Quality and Use*. 1st Edn., Springer Science and Business Media, Berlin, ISBN-10: 3642564143, pp: 315.
- Lakshmanan, E., R. Kannan and M.S. Kumar, 2003. Major ion chemistry and identification of hydrogeochemical processes of groundwater in a part of Kancheepuram district, Tamil Nadu, India. *J. Environ. Geosci.*, 10: 157-166.
- Lund, J.W., 2000. Balneological use of thermal water in the USA, *GHC Bull.*
- Makungo, R., J.O. Odiyo, J.G. Ndiritu and B. Mwaka, 2010. Rainfall-runoff modelling approach for ungauged catchments: A case study of Nzhelele River sub-quadernary catchment. *Phys. Chem. Earth*, 35: 596-607.
- Makwe, E. and C.D. Chup, 2013. Seasonal variation in physicochemical properties of groundwater around Karu abattoir. *Ethiopian J. Environ. Stud. Mgt.*, 6: 489-497
- Mazor, E. and B.T Verhagen, 1983. Dissolved ions, stable and radioactive isotopes and noble gases in thermal waters of South Africa. *J. Hydrol.*, 63: 315-329.
- Mondal, N.C., V.P Singh and V.S Singh, 2010. Saxena VK, Determining the interaction between groundwater and saline water through groundwater major ions chemistry. *J. Hydrol.*, 388: 100-111.
- Odiyo, J.O. and R. Makungo, 2012. Fluoride concentrations in groundwater and impact on human health in Siloam Village, Limpopo Province, South Africa. *Water SA.*, 38: 731-736.
- Olivier, J., H.J. Van Niekerk and I.J.V.D. Walt, 2008. Physical and chemical characteristics of thermal springs in the Waterberg area of Limpopo Province, South Africa. *Water SA*, 34: 163-174.
- Olivier, J., J.S Venter and H.J.V. Niekerk, 2010. Physical and chemical characteristics of thermal springs in Limpopo province, South Africa. *Proceedings of the World Geothermal Congress, (WGC' 10)*, Bali, Indonesia.
- Olivier, J., J.S., Venter and C.Z. Jonker, 2011. Thermal and chemical characteristics of thermal springs in the Northern part of the Limpopo Province, South Africa. *Water SA*, 34: 163-174.
- Petraccia, L., G. Liberati and S.G. Masciullo, 2005. Water, mineral waters and health. *Clin. Nutrit.*, 25: 377-385.
- Piper, A.M., 1944. A graphic procedure in geochemical interpretation of water analyses. *Trans. Am. Geophys. Union*, 25: 914-923.
- Press, F. and R. Siever, 1986. *Earth*. 4th Edn., W.H. Freeman and Company, New York.
- Raghunath, H.M., 1987. *Groundwater*. 1st Edn., Wiley Eastern Limited, New Delhi, pp: 563.
- Rajesh, R., K. Brindha, R. Murugan and L. Elango, 2010. Influence of hydrogeochemical processes on temporal changes in groundwater quality in a part of Nalgonda district, Andhra Pradesh, India. *Environ Earth Sci.*
- Ramesh, K. and L. Elango, 2011. Groundwater quality and its suitability for domestic and agricultural use in Tondiar river basin, Tamil Nadu. *India Environ Monit. Assess.* DOI 10.1007/s10661-011-2231-3
- Sajil Kamar, P.J., 2013. Interpretation of groundwater chemistry using Piper and Chadha's diagrams: A comparative study from perambalur taluk. *Elixir Geosci.*, 54: 12208-12211.
- Schiavo, M.A., S. Havser, G. Gusimano and L. Gatto, 2006. Geochemical characterisation of groundwater and submarine discharge in the south-eastern Sicily. *Continental Shelf Res.*, 26: 826-834.
- Schoeller, H., 1977. *Geochemistry of groundwater*. *Proceedings of the Groundwater Studies – An international Guide for Research and Practice, (GRP' 77)*, Paris, pp: 1-18.
- Smith, M. and L. Puczko, 2009. *Health and Wellness Tourism*. 1st Edn., Elsevier, Tokyo.
- SABS, 1999. Class 1 potable water standards. SABS 241:1999. South African Bureau of Standards Pretoria, South Africa.
- Subramani, T. and L. Elango, 2005. Damodarasamy, SR, Groundwater quality and its suitability for drinking and agricultural use in Chithar River Basin, Tamil Nadu, India. *Environ. Geol.*, 47: 1099-1110.
- USEPA, 1994. Method 200.8. Determination of trace elements in waters and wastes by ICP, Revision 5.4. United State Environmental Protection Agency
- USEPA, 2004. Guideline for water reuse. EPA, Washington DC, EPA/625/R-04/108. United State Environmental Protection Agency.
- USEPA, 1993. Rev 2.1, Determination of inorganic anion in water by ion chromatography, US environmental agency, Cincinnati, OH.
- Van Vuuren, K. 1990. *Die Warmwaterbronne van Suidwes-Kaapland: Hulle Verbreiding, Eienskappe en Benutting*. B.A. Honours dissertation, University of Stellenbosch, South Africa.
- Vassileva, S., 1996. Mineral water and spas in Bulgaria, *Clinics in Dermatology*, 14.
- Vimmerstedt, L.T., 1998. Opportunities for small geothermal projects: Rural power for Latin America, the Caribbean and the Philippines. Natural renewable energy laboratory, Colorado, USA.
- Wilcox, L.V., 1958. *Classification and use of irrigation water*. US Department of Agriculture, Circular 969, Washington, DC

- WHO, 1989. Health guidelines for use of wastewater in agriculture and aquaculture. WHO Geneva.
- WHO, 2000. Bottled drinking water.
- Yahaya, M.I., S. Mohammad and B.K. Abdullahi, 2009. Seasonal variations of heavy metal concentration in Abattoir dumping site soil in Nigeria. *J. Applied Sci. Environ. Manage.*, 13: 9-13.