Hydrogeochemistry of the Kasane Hot Spring, Botswana

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Abstract The hydrogeochemistry of the Kasane hot spring in Kasane was conducted with the aim of knowing the hydrochemical nature of the spring. Kasane is situated in the most northern part of Botswana within the Chobe District. Sixteen water samples, forty-nine sediment samples and five rock samples were collected for analyses to achieve this objective. The water and sediment samples were analyzed for major cations, major anions and trace elements at the geochemistry laboratories of the University of Botswana and at the Department of Water Affairs. The physico-chemical parameters such as temperature of the water, pH, EC and TDS were measured in-situ. Petrographic analysis of the rock thin sections was also carried out to identify the mineralogical composition of the rocks of the study area. The geology of the area is generally Karoo volcanic. Thin sections analyses revealed that the rock is basalt made up of plagioclase, clinopyroxene and opaque minerals with orthopyroxene and amphibole in trace amounts. In the analyzed water samples generally based on the mean values of the chemical parameters, the cations were in the order of abundance as $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Li}^+$ and the anions were in the order of abundance as $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{PO}_4^{3-} > \text{Br}^- > \text{CO}_3^{2-} > \text{NO}_3^- > \text{F}^- > \text{NO}_2^-$. In the analysed sediment samples the cations and anions are in the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+} > \text{Li}^+$ and $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^- > \text{Br}^- > \text{NO}_2^- > \text{PO}_4^{3-}$, respectively. The spring and the groundwater from the pits north of the spring are slightly alkaline to alkaline, brackish to saline and hard to very hard whereas the groundwater west of the springs, river water and the sewage water are acidic to slightly alkaline (with the exception of sample W11, which is alkaline), fresh (with the exception of sample W12, which is brackish) and soft to hard. 75 % of the analyzed groundwater samples from the pits west of the hot spring show some similarities in the trend of concentration of the different constituents of the groundwater with the river water, suggesting that the groundwater is recent or derived from precipitation. The remaining 25 per cent of the groundwater samples from this part of the study area suggest that precipitation is not the sole source of groundwater and it could be derived from both precipitation and fluids of deep origin. The hot spring and the groundwater north of the hot springs are characterized by higher mineralization, and this could be attributed to the more supplement of the deep fluids that have deep origin.

This implies that the source of the spring and the groundwater north of the hot spring have a regional origin. The hot spring water and all groundwater in the studied area are not recommended for drinking purposes.

Keywords Deep Fluids, Groundwater, Hot Spring, Hydrogeochemistry, Kasane

1 Introduction

1.1. General

Water with good quality and sufficient quantity from different resources is a backbone for economic development of a country [1]. However, according to the Botswana Water Statistics report [2], Africa's water resources are threatened by the increasing population trends which result in increase in water demand by various users. In Botswana, this very precious resource is scarce due to the semi-arid climatic condition of the country which is characterized by recurrence of drought.

A spring is a concentrated discharge of groundwater appearing at the ground surface as current flowing water [3]. It may have a fairly constant or variable discharge. It may be permanent or it may be temporary. It will contain dissolved solids in the form of ions or certain dissolved gases or oils like petroleum. It may be hot or it may have a temperature that is very low.

Generally thermal springs, also referred to as hot springs, are located all over the world at special geological areas, mainly near volcanic regions. Thermal springs are by definition 'warm'; however, there is no consensus regarding the exact temperature that distinguishes a spring from a thermal spring [4]. In view of the fact that the climate of one region differs from that of another, what is 'warm' in one region may not be considered to be such elsewhere. For this reason, the definition of a thermal spring is often based on the mean annual air temperature of the specific site [4].

According to LaMoreaux and Tanner [5], thermal springs originate either from recent plutonic activity (volcanic origin) or from rainwater that percolates into the ground through permeable rocks or via conduits such as joints, faults and fracture zones in less permeable rocks

(meteoric origin). Such water may reach considerable depths before resurfacing.

Like all natural resources, thermal springs should be managed in a sustainable manner. The availability of current scientific information on thermal springs and their properties is a pre-requisite for sound decision making regarding resource use and development. Unfortunately, there has not been any hydrogeochemical study of hot springs in Kasane. This research, which makes its objective to determine the hydrogeochemical features of the Kasane hot spring and the groundwater in its surrounding areas, and determine their suitability for drinking purpose, presents, for the first time, information on thermal springs located in the northern part of the country at Kasane in the Chobe District.

1.2. Description of the Study Area

1.2.1. Location

The study area is situated in the northern part of Botswana at Kasane in the Chobe District. Chobe District (22, 560 km²) is one of the smallest districts in Botswana and has an international setting. It is where Botswana meets Namibia, Zimbabwe and Zambia. Kasane is a few kilometers from the Chobe River's confluence with the Zambezi River and lies within the lines of longitude of 24°

and 26° E, and latitude of 17° and 19° S (Fig 1).

1.2.2. Topography and Drainage

The Chobe district in general is made up of a relatively featureless central plateau and floodplains in the north and west of the district. The whole study area drains toward the Chobe River. The Chobe River rises as the Cuando in the highlands of Angola. When it crosses into Botswana, it becomes the Linyanti, at Parakarungu it becomes the Itenge, and at Ngoma Gate it becomes the Chobe River. Finally, it joins the Zambezi at Kazungula after which they hurtle together over Victoria Falls.

The studied area consists of only one hot spring issue from the alluvial sediments in the floodplain. According to the information from the elder peoples in the community, there were other hot springs in the area. However, at present these hot springs do not exist anymore, and nobody knows when they disappeared or where the exact positions of the springs were.

The climate in Kasane is referred to as a local steppe climate or a hot semi-arid steppe climate. In a year, the average rainfall is 643 mm. Generally, the annual rainfall varies between 550 mm and 650 mm being the highest in the country and the least variable. Over the course of a year, the temperature typically varies from 9 °C to 35 °C.

Figure 1. Location of the study area.

1.2.3. Geology of the Study Area

1.2.3.1. Local Geology

The local geology is comprised of the Karoo Supergroup rocks. The Kalahari Basin is amongst the several contemporaneous basins in southern Africa which covers an extensive area in Botswana (Fig 2). The Kalahari basin is contiguous to the Mid-Zambezi basin which is located in the northwestern part of Zimbabwe. The boundary between the two basins is not well defined. The top most geologic unit in the Kalahari Basin is the basalt of the Stormberg Lava Group [6]. Based on the stratigraphic section obtained in the eastern part of the Kalahari basin, the Stormberg Lava Group is underlain by the sandstone of Ntane Formation which in turn overlie the Mosolotsane Formation which is essential made up of arenaceous sediments of fluvial origin. Below the Mosolotsane Formation is the Tlhabala Formation which conformably overlies the Tlapana Formation. The Tlapana Formation is comprised of mudstones, carbonaceous shales and coal seams. It overlies the Mea arkose Formation which is generally composed of pebbly sandstones and conglomerates [7].

The adjacent Mid-Zambezi basin contains a thick basaltic rock at the top which belong to the Batoka Formation. The basalt is underlain by the Forest Sandstone Formation comparable to the Ntane Formation. Below the Forest Sandstone occurs the pebbly arkose and fine red marly sandstone with ripple marked flagstone at the bottom. This unit is a correlative of the Mosolotsane Formation [6]. It is important to note that the study area (Kasane) is located mid-way between the Kalahari and Mid-Zambezi basins (Fig 2). Though the area is considered to be part of the Kalahari basin, there is no lithostratigraphic data from the area to confirm the stratigraphic column of the Karoo sequence in the area since there are no boreholes drilled in the area or in the vicinity of the area in Botswana.

Figure 2 Map showing the Karoo basins in the study area (modified from Johnson et al., 1996).

2. Methodology

In order to determine the hydrogeochemistry of the

Kasane hot spring, representative water, sediment and rock samples were collected during the rainy season. Analyses of the water and sediment samples were carried out both in the geochemistry laboratory of the University of Botswana and in the laboratory of the Department of Water Affairs of Botswana. Cations and trace elements of the water and sediment samples were analysed in the geochemistry laboratory of the University of Botswana. Anions of the water samples were analysed in the laboratory of the Department of Water Affairs of Botswana. Anions of the sediments samples were analysed in the geochemistry laboratory of the University of Botswana. Rock samples were characterized by studying thin-sections at the transmitted light microscope.

2.1. Data Collection

Sixteen (16) water samples, forty nine (49) sediment samples and five (5) rock samples were collected from different sites of the studied area.

The water samples were collected from the hot spring, sewage ponds, the river and the pits: one from hot spring, two from sewage ponds, one from the nearby river water and 12 from the drilled pits. The pits, which were drilled for sediment sampling purposes, were drilled in different directions and at different intervals from the spring; because of this reason, with the exception of the hot spring sample all the water samples from the pits were obtained from the same points where sediment sampling was done. The pits had a dimension of 30 cm by 30 cm and depth of 50cm. One kilogram (kg) sediment samples were collected from each pit using a plastic bag. The positions and altitudes of the pits were determined using Global Positioning System (GPS).

The sediments were obtained from all directions (north, south, east and west) of the spring at a distance of an interval of 50m with the spring as the point of origin. Since the pits east and south of the hot spring were dry and did not yield any water the water samples were obtained only from north and west of the of spring. The two sewage ponds are located in the upstream side of the hot spring, while the river is located in the downstream side of the spring. The river is of a perennial type.

The water samples were collected in one litre Polyethylene terephthalate bottles after filtered them through 0.45- μ m cellulose filters. Prior to sampling the bottles were rinsed with samples to be collected. In the field in situ measurements of the water temperature, pH, EC, and TDS were conducted using digital multi-parameter analyser model Hanna. The positions and altitudes of the sampling points (locations) were also determined using Global Positioning System (GPS).

Representative rock samples were also collected during the field work from the outcrops. The positions and altitudes of the sampling points (location) determined using Global Positioning System (GPS). Thin-sections of

the rocks samples were prepared in the University of Botswana at the cutting and polishing laboratory of the Department of Geology for petrographic investigation.

2.2. Data Analyses

1. Water samples

The water samples were analyzed for calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+), lithium (Li^+), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), fluoride (F^-), phosphate (PO_4^{3-}), nitrite (NO_2^-) and bromine (Br^-). The trace element that were analysed in the water samples were arsenic (As), barium (Ba), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), lead (Pb), nickel (Ni) and zinc (Zn). The water from sewage ponds, river and pits were analyzed for comparison with hot spring water.

All cations and trace elements were analysed using ICP-MS. The method applied for the analysis of anions was ISO 10304 using the ion chromatography. The alkalinity and hardness of water samples were determined using AquaChem software.

In the water analyses, for analytical precision of measured samples, charge balance was calculated using the following equation:

Where, E.N (%) =

$$= \left[\frac{(\text{Sum cations} - \text{Sum anions})}{(\text{Sum cations} + \text{Sum anions})} \right] * 100 \quad (1)$$

All the measurements are in milli equivalents per litre.

Simple descriptive statistical method was utilized for the analyses of the groundwater chemistry data. Besides, AquaChem software was used to process water geochemical data. Piper diagram was prepared to represent and compare water quality data in the area. Gibbs diagram was also used to see the relationship of water composition and aquifer lithological characteristics.

2. Sediments samples

The soil samples were analyzed for calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+), and lithium (Li^+), chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), fluoride (F^-), phosphate (PO_4^{3-}), nitrite (NO_2^-) and bromine (Br^-). The trace element that were analysed in the soil samples were arsenic (As), barium (Ba), cadmium (Cd), Cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), lead (Pb), nickel (Ni) and zinc (Zn). Simple descriptive statistical method was used for the analyses of the soil chemistry data too.

3. Rock samples

The rock samples were preliminarily characterized by studying the hand specimen. Thereafter, thin-sections of

the rock samples were observed for minerals at the transmitted light microscope using Nikon Eclipse 50i POL microscope at the petrological laboratory of the Department of Geology in the University of Botswana in order to establish the relationship between the geology and the chemistry of the water in the study area.

3. Results and Discussions

3.1. Results

3.1.1. Physico-chemical Parameters

The water is acidic to alkaline and soft to very hard pH ranges from 6.33 to 9.12 with an average of 7.27. The maximum value of pH was measured 750 m west of the spring and minimum was measured in the center of the river. Electrical conductivity and total dissolved solids range from $82\mu\text{S}/\text{cm}$ to $22320\mu\text{S}/\text{cm}$ and 36.72 mg/l to 14476.92 mg/l with a mean value of $5172.75\mu\text{S}/\text{cm}$ and 3140.72 mg/l , respectively. The highest electrical conductivity value is $22320\mu\text{S}/\text{cm}$ measured 50m north of the spring. From north side of the spring all the measured electrical conductivity values are above $10000\mu\text{S}/\text{cm}$. The measured electrical conductivity values west of the spring and at the sewage have low values mostly below $1500\mu\text{S}/\text{cm}$. The temperature of the water samples was recorded between 25°C and 49.7°C with an average value of 28.99°C . The maximum temperature was measured in the spring and the lowest was 1197.5m west of the spring.

3.1.2. Hardness and Alkalinity

The hardness of the water in the study area varies from soft to very hard. All the water samples north of the hot spring reveal that the water is very hard to hard whereas the water samples west of the hot spring indicates that water is soft. The sewage water from upstream side, which is south of the hot spring, and the river water from downstream side are both soft water.

The alkalinity of the water samples range from 31.58 to 446.92 mg/l of CaCO_3 . Very high values are observed north of the hot springs and in one of the sewage sample. The result indicates that all the waters of the studied area are less susceptible to acidification.

3.1.3. Water Type

The chemical analysis results of the water samples from the study area are plotted in Piper diagram using Aquachem software (Fig 3). Accordingly, with the exception of the sewage water and one water sample from west of the hot spring, three major water types are recognized in the studied area: Ca-Mg-Na-HCO_3 , Na-Cl-SO_4 , and $\text{Na-SO}_4\text{-Cl}$; constituting 38%, 31%, and 13% of the total water samples, respectively. The two sewage water samples are $\text{Na-HCO}_3\text{-Cl}$ and

Na-Cl-HCO₃-SO₄ types, while one sample from west of the hot spring shows Ca-Mg-HCO₃.

Figure 3. Piper plot for the water samples

3.1.4. Major Ions Compositions

The summarized results of the chemical composition of the analyzed water samples are given in Table 1 below.

The dominant cations in the water samples are sodium and calcium. The concentration of Na⁺ ranges from 3.491 mg/l to 4308 mg/l having a mean value of 1042.12 mg/l. K⁺ ranges from 1.493 mg/l to 25.42 mg/l with a mean value of 8.869 mg/l. Ca²⁺ ranges from 5.01 mg/l to 349.8 mg/l with a mean value of 70.4709 mg/l while Mg²⁺ ranges from 2.791 mg/l to 41.72 mg/l with a mean value of 10.869 mg/l. Cation content indicates that 43.75 % of the water samples follows the following trend; Ca²⁺ > Na⁺ > Mg²⁺ > K⁺ > Li⁺. The remaining samples follow 5 different trends; 18.75% shows Na⁺ > Ca²⁺ > K⁺ > Mg²⁺ > Li⁺; 18.75% of the samples shows Na⁺ > Ca²⁺ > Mg²⁺ > K⁺ > Li⁺; and, the last 3 samples which take up 6.25 % of the total number of samples are each unique and follow the following trends Na⁺ > Mg²⁺ > Ca²⁺ > K⁺ > Li⁺, Na⁺ > K⁺ >

Ca²⁺ > Mg²⁺ > Li⁺ and Na⁺ > K⁺ > Mg²⁺ > Ca²⁺ > Li⁺. Generally, based on the mean values of the chemical parameters, the cations were in the order of abundance as Na⁺ > Ca²⁺ > Mg²⁺ > K⁺ > Li⁺.

Among anions, HCO₃⁻ ranges from 38.5 mg/l to 544.9 mg/l with mean value of 167.044 mg/l while CO₃²⁻ ranges from 0 mg/l to 25.2 mg/l with mean value of 2.413 mg/l. The concentration of SO₄²⁻ ranges from 2.39 mg/l to 6369.31 mg/l with a mean value of 1469.98 mg/l while Cl⁻ ranges from 1.93 mg/l to 7570.65 mg/l with mean value of 1505.72 mg/l. The concentration of NO₃⁻ ranges from 0 mg/l to 20.23 mg/l with mean value of 2.4 mg/l while NO₂⁻ ranges from 0 mg/l to 0.05 mg/l with mean value of 0.009 mg/l. F⁻ ranges from 0.02 mg/l to 5.36 mg/l with mean value of 1.354 mg/l. PO₄³⁻ concentration ranges from 0 mg/l to 45.6 mg/l with mean value of 3.55 mg/l. Generally based on the mean values of the chemical parameters, the anions were in the order of abundance as Cl⁻ > SO₄²⁻ > HCO₃⁻ > PO₄³⁻ > Br⁻ > CO₃²⁻ > NO₃⁻ > F⁻ > NO₂⁻.

There is a variation of chloride concentrations of the water samples with the lowest concentration observed from the river and the highest observed 50m north of the spring. The chloride concentration increases towards the spring from both the north and west directions. However, the concentration is lowest in the river sample.

The samples obtained from the spring and from north of the spring measured the highest levels of sulphate compared to the rest of the samples. These concentrations were all above 2000mg/l. Lower concentration levels were obtained mostly from samples west of the spring.

The highest nitrate level was from the sewage water sample. Generally, the nitrate concentration decreased towards the spring from the directions which were analyzed for nitrates (west and north).

Table 1. Summarized results of the analyzed water samples (mg/l).

ID	Type/direction*	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	F ⁻	CO ₃ ²⁻	HCO ₃ ⁻	NO ₂ ⁻	PO ₄ ³⁻	Br ⁻	Ca ²⁺	K ⁺	Li ⁺	Mg ²⁺	Na ⁺
W1	Hot spring	3452.21	3398.47	1.05	2.96	0	110.4	0	0	7.95	151.74	15.664	0.4759	12.94	1983.6
W2	50m N	7570.65	6369.31	0	3.63	0	544.9	0	0	15.43	349.8	25.42	0.6286	36.22	2649
W3	100m N	5321.91	5047.33	1.87	3.03	0	316.2	0	0	10.8	294.81	19.868	0.5451	24.92	4308
W4	150m N	3321.67	3321.26	0.3	5.11	0	406.4	0	0	7.78	154.82	15.96	0.4307	9.989	3105
W5	200m N	3069.53	2921.92	6.97	5.36	13.4	285.6	0	0	6.97	67.34	16.694	0.4296	6.756	2882
W6	300m W	2.43	3.22	0.42	0.02	0	40.7	0.05	0	0.004	7.287	2.052	0.0021	3.483	5.847
W7	350m W	2.21	3.09	0.46	0.04	0	40.9	0.03	0	0.02	5.812	1.694	0.0015	3.208	3.82
W8	400m W	2.22	3.44	0.35	0.03	0	40.5	0	0	0.001	5.554	1.493	0.0015	3.085	3.966
W9	500m W	2.04	2.92	0.37	0.03	0	38.5	0.03	0	0	5.484	1.615	0.0016	3.119	3.491
W10	550m W	3.02	2.98	0.43	0.05	0	42.5	0.01	0	0	5.633	1.563	0.0022	3.116	3.504
W11	750m W	167.74	317.83	0.59	0.4	25.2	90.8	0	0	0.19	18.886	9.467	0.0411	9.677	186.28
W12	1050m W	935.27	2078.69	3.88	0.36	0	120.4	0	0	1.65	36.04	2.457	0.0128	41.72	1349
W13	1197.5m W	2.32	2.39	0.42	0.04	0	39.7	0.03	0	0	5.346	1.638	0.0015	3.106	3.634
W14	River random	1.93	2.72	0.34	0.03	0	40.1	0	0	0	5.45	1.601	0.0016	3.187	3.696
W15	Sewage 1	183.93	2.97	0.72	0.47	0	427	0	45.6	0.14	8.523	10.476	0.0027	2.791	134.62
W16	Sewage 2	52.48	41.17	20.23	0.1	0	88.1	0	11.2	0.02	5.01	14.24	0.0061	6.58	48.46
Minimum		1.93	2.39	0	0.02	0	38.5	0	0	0	5.01	1.493	0.0015	2.791	3.491
Maximum		7570.65	6369.31	20.23	5.36	25.2	544.9	0.05	45.6	15.43	349.8	25.42	0.6286	41.72	4308
Mean		1505.72	1469.98	2.4	1.354	2.413	167.044	0.009	3.55	3.185	70.4709	8.86888	0.16154	10.8686	1042.12

*: Direction and distance from the hot spring.

3.1.5. Trace Elements

The results of the analyzed trace elements is summarized and given in the Table 2 below. Among the analyzed trace elements, Ni is the dominant constituent. Its concentration ranges from 0.3219 mg/l to 2.288 with mean value of 0.95 mg/l. Fe, Pb, Mn, Zn, and Ba are the major trace elements that are found constituting the water following Ni having concentration of 0.12 mg/l, 0.08mg/l, 0.05mg/l, 0.03mg/l and 0.03mg/l, respectively. As, Cd, Co, Cr and Cu are found having concentration less than 0.001 mg/l.

Table 2. Summarized results of some of the analyzed trace elements in water samples (mg/l).

ID	Type/Direction*	As	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
W1	Hot spring	0.0001	0.0134	0.0055	0.0014	0.001	0.0043	0.0014	0.0893	1.652	0.165	0.041
W2	50m N	0.0033	0.0354	0.0075	0.0029	0.0001	0.0041	0.0249	0.5172	2.228	0.0819	0.0396
W3	100m N	0.0032	0.053	0.0052	0.0004	0.0004	0.0034	0.0062	0.0076	0.8354	0.0865	0.0334
W4	150m N	0.0097	0.0257	0.0102	0.0013	0.0002	0.0034	0.0036	0.0491	2.288	0.0362	0.0493
W5	200m N	0.0067	0.028	0.0034	0.0004	0.0005	0.0014	0.0019	0.0713	1.766	0.0671	0.0423
W6	300m W	0.0061	0.025	0.0011	0.0018	0.0005	0.0027	0.0787	0.003	0.4447	0.1	0.0305
W7	350m W	0.001	0.0242	0.0024	0.0004	0.0002	0.0046	0.2102	0.001	0.424	0.032	0.0291
W8	400m W	0.001	0.0234	0.0062	0.0035	0.0002	0.0044	0.2517	0.0009	0.4666	0.2121	0.0214
W9	500m W	0.0037	0.0187	0.0033	0.0025	0.0002	0.004	0.0509	0.0003	0.4225	0.1114	0.0302
W10	550m W	0.0005	0.0278	0.0077	0.0013	0.0015	0.0043	0.6987	0.0017	0.5858	0.0252	0.0263
W11	750m W	0.004	0.0202	0.0107	0.0011	0.0004	0.0025	0.0168	0.0003	1.13	0.0297	0.0324
W12	1050m W	0.0007	0.0539	0.0038	0.0001	0	0.0036	0.0057	0.0002	0.3219	0.0247	0.0436
W13	1197.5m W	0.0014	0.0234	0.0021	0.0018	0	0.0046	0.3013	0.0011	0.4779	0.0143	0.0227
W14	River random	0.0034	0.0248	0.0032	0.0004	0.0001	0.0045	0.1525	0.0006	0.4873	0.0627	0.0029
W15	Sewage 1	0.0036	0.0028	0.0181	0	0.0002	0.0024	0.0292	0.0014	0.7496	0.028	0.0424
W16	Sewage 2	0.0018	0.028	0.0035	0.0023	0.0001	0.0031	0.0099	0.0015	0.8402	0.1546	0.0341
Minimum		0.0001	0.0028	0.0011	0	0	0.0014	0.0014	0.0002	0.3219	0.0143	0.0029
Maximum		0.0097	0.0539	0.0181	0.0035	0.0015	0.0046	0.6987	0.5172	2.288	0.2121	0.0493
Mean		0.00314	0.02673	0.00587	0.00135	0.00035	0.00358	0.11523	0.04666	0.94499	0.07696	0.03258

*: Direction and distance from the hot spring.

3.1.6. Sediments

As it was mentioned in the methodology parts, the sediments were analyzed for major cations, major anions and some trace elements. The same cations and trace elements that were analyzed for the water samples were also analyzed in the sediment samples and with exception of bicarbonate and carbonate, seven of the anions analyzed in the water samples were also analyzed in the sediments samples. The data generated for the sediment samples are given in Table 3, 4 and 5 and are discussed below.

The results of the analysis indicate that the concentration of Na^+ ranges from 0.1 mg/l to 25.34 mg/l with mean value of 3.438 mg/l and K^+ ranges from 0.494 mg/l to 11.66 mg/l with mean value of 2.650 mg/l. Ca^{2+} ranges from 0.1387 mg/l to 37.7 mg/l with mean value of 3.067 mg/l while Mg^{2+} ranges from 0.111 mg/l to 7.21 mg/l with mean value of 1.436 mg/l. Li^+ ranges from 0.003 mg/l to 0.046 mg/l with mean value of 0.010 mg/l. Based on the mean values of the chemical parameters, the cations were in the order of abundance as $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+} > \text{Li}^+$.

The analysis of the anions indicates that there is no PO_4^{3-} and NO_2^- present in the sediment samples. The concentrations of F^- range from 0 mg/l to 1.463 mg/l with a mean value of 0.232 mg/l. Cl^- concentrations range from 0.622 mg/l to 923.5 mg/l with a mean value of 84.103 mg/l. Br^- concentration was only present in only one sample and therefore ranged from 0 mg/l to 1.626 mg/l with a mean value of 0.068 mg/l. The concentrations of NO_3^- range from 0 mg/l to 10.064 mg/l with a mean value of 1.116 mg/l. SO_4^{2-} concentrations range from 0 mg/l to 1883.9 mg/l with a mean value of 347.44 mg/l. Based on the mean values of the chemical parameters, the anions were in the order of abundance as $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^- > \text{Br}^- > \text{NO}_2^- > \text{PO}_4^{3-}$.

Table 3. Summarized results of the analyzed sediment samples for cations (mg/l).

ID	Direction*	Ca^{2+}	K^+	Li^+	Mg^{2+}	Na^+
S1	50m N	10.66	11.66	0.046	4.88	17.65
S2	100m N	7.51	6.093	0.0286	2.873	25.34
S3	150m N	0.5537	0.6386	0.0038	0.1604	1.357
S4	200m N	1.049	2.416	0.0105	1.007	0.9379
S5	50m E	0.5376	1.228	0.0042	0.1516	1.009
S6	100m E	0.5349	2.655	0.0088	0.5572	0.9928
S7	150m E	1.176	3.547	0.022	1.971	4.054
S8	200m E	18.23	8.844	0.0295	5.93	10.9
S9	250m E	9.749	4.948	0.0161	3.574	6.363
S49	300m E	2.633	2.705	0.0135	1.666	3.87
S10	350m E	6.972	2.733	0.0148	2.177	2.805
S11	400m E	1.845	3.132	0.0117	2.103	4.135
S12	450m E	3.081	3.914	0.0146	3.23	3.317
S13	500m E	3.653	3.813	0.0123	3.182	4.857
S14	550m E	5.4	3.751	0.0162	4.543	7.813
S15	600m E	37.7	3.674	0.0222	7.21	6.795
S16	50m S	1.808	5.008	0.0086	0.7586	3.305
S17	100m S	0.7566	1.722	0.0037	0.3735	2.464
S18	150m S	0.7597	1.695	0.0035	0.3651	2.424
S19	200m S	5.294	7.182	0.0179	3.718	8.678
S20	250m S	3.174	3.389	0.0049	1.139	2.627
S21	300m S	3.968	4.71	0.0112	2.616	4.556
S22	350m S	4.657	3.747	0.0111	2.477	6.7
S23	400m S	2.307	5.233	0.0121	3.153	4.783
S24	450m S	2.485	4.565	0.0081	2.472	2.146
S25	50m W	0.7858	2.298	0.0049	0.648	3.268
S26	100m W	0.1902	0.7339	0.0032	0.1872	3.27
S27	150m W	0.4219	1.311	0.004	0.4011	0.4777
S28	200m W	0.2197	0.6479	0.0027	0.2204	0.14
S29	250m W	0.1879	0.6725	0.0029	0.2282	0.26
S30	300m W	0.2723	0.7119	0.0029	0.1696	0.5794
S31	350m W	0.1387	0.5919	0.0026	0.1621	0.1
S32	400m W	0.1481	0.6259	0.0026	0.1734	0.206
S33	450m W	0.3064	0.9063	0.0041	0.2325	0.433
S34	500m w	0.2523	1.033	0.0043	0.2479	0.14
S35	550m w	0.8739	1.673	0.0073	0.7639	4.151

S36	600m W	3.83	1.47	0.0094	0.7384	3.831
S37	650m W	1.393	1.534	0.0069	0.5975	3.785
S38	700m W	0.3154	1.109	0.005	0.31	1.337
S39	750m W	2.286	1.806	0.0161	1.082	2.609
S40	800m W	0.319	1.361	0.0047	0.2746	0.7636
S41	850m W	0.2118	1.073	0.0032	0.1398	0.6649
S42	900m W	0.2289	0.9547	0.0039	0.1999	0.4135
S43	950m W	0.1728	1.065	0.004	0.2153	0.3268
S44	1000m W	0.2904	1.361	0.0048	0.274	0.4302
S45	1050m W	0.1867	1.119	0.0038	0.1767	0.365
S46	1100m W	0.2518	1.092	0.004	0.2094	0.3574
S47	1150m W	0.3527	1.166	0.0046	0.2927	0.4781
S48	1197.5m W	0.15	0.4936	0.003	0.1113	0.2163
Minimum		0.1387	0.4936	0.0026	0.1113	0.1
Maximum		37.7	11.66	0.046	7.21	25.34
Average		3.066922	2.649229	0.009608	1.435578	3.4384

*: Direction and distance from the hot spring.

Table 4. Summarized results of the analyzed sediment samples for anions (mg/l).

ID	Direction*	PO ₄ ³⁻	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻
S1	50m W	0	0.61	109.4	0	0	1.485	84.624
S2	100m W	0	0	1.754	0	0	0	0
S3	150m W	0	0	2.477	0	0	0	1.992
S4	200m W	0	0	0.622	0	0	0	0
S5	300m W	0	0	45.6	0	0	0	35.076
S6	400m W	0	0	0.855	0	0	0	0
S7	500m W	0	0	1.165	0	0	0	0
S8	50m N	0	0	275.6	0	0	0	1883.9
S9	100m N	0	1.462	923.5	0	1.626	0	901.5
S10	150m N	0	0	44	0	0	1.888	42.251
S11	200m N	0	0	2.136	0	0	3.305	15.594
S12	50m S	0	0	26.4	0	0	0	217.8
S13	100m S	0	0	23.4	0	0	0	866.3
S14	150m S	0	0	118.5	0	0	0	144.972
S15	200m S	0	0.705	121	0	0	0	1529.4
S16	300m S	0	1.212	9.231	0	0	1.479	616.2
S17	400m S	0	0.447	35.1	0	0	0	90.46
S18	50m E	0	0	74.3	0	0	10.064	60.555
S19	100m E	0	0	1.724	0	0	0	0
S20	150m E	0	0.65	29.7	0	0	3.372	145.402
S21	200m E	0	0	20.7	0	0	1.619	692.9
S22	300m E	0	0	33.4	0	0	0	428.6
S23	400m E	0	0	75.7	0	0	0	480.7
S24	500m E	0	0.476	42.2	0	0	3.583	100.234
Minimum		0	0	0.622	0	0	0	0
Maximum		0	1.462	923.5	0	1.626	10.064	1883.9
Average		0	0.23175	84.10267	0	0.06775	1.116458	347.4358

*: Direction and distance from the hot spring.

Among the analyzed trace elements Fe, Ni and Pb have dominant concentrations: the concentration of Fe ranges from 1.74 mg/l to 51.96 mg/l with mean value of 14.019 mg/l, Ni ranges in concentration from 0.002 mg/l to 1.163 mg/l with mean value of 0.316 mg/l and the concentration of Pb ranges from 0.026 mg/l to 0.827 mg/l with mean value of 0.278 mg/l. All the remaining analyzed trace elements have a mean concentration below 0.2 mg/l. Based on the mean values of the chemical parameters, the trace elements were in the order of abundance as Fe > Ni > Pb > Ba > Mn > Zn > As > Cu > Cr > Co > Cd.

Table 5. Summarized results of the analyzed sediment samples for some trace elements (mg/l).

ID	Direction*	As	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
S1	50m N	0.2211	0.6208	0.0676	0.0677	0.0807	0.1412	51.96	0.5508	0.1093	0.4786	0.2677
S2	100m N	0.4689	0.2829	0.0447	0.0298	0.0429	0.0551	26.51	0.3214	0.0332	0.3551	0.0413
S3	150m N	0.1621	0.0446	0.0109	0.0082	0.0134	0.0046	2.409	0.0767	0.5632	0.2887	0.0049
S4	200m N	0.0035	0.1363	0.0067	0.0143	0.03	0.0107	9.894	0.0782	0.138	0.4315	0.1133
S5	50m E	0.006	0.0968	0.0005	0.0086	0.0109	0.0045	1.74	0.0345	0.0591	0.2141	0.0444
S6	100m E	0.0059	0.1451	0.0021	0.0141	0.0146	0.0116	6.865	0.0839	0.2935	0.6802	0.1997
S7	150m E	0.1541	0.2015	0.0173	0.0245	0.0302	0.0259	16.86	0.1665	0.2609	0.674	0.0984
S8	200m E	0.0505	0.4149	0.0143	0.0327	0.0451	0.0681	33.13	0.3105	0.0347	0.4694	0.1564
S9	250m E	0.1703	0.3226	0.0199	0.0318	0.0455	0.0684	29.22	0.2797	0.2316	0.4339	0.0012
S49	300m E	0.136	0.3907	0.0147	0.0185	0.0459	0.0388	19.43	0.2441	0.1039	0.1874	0.0707
S10	350m E	0.0361	0.1854	0.0082	0.0196	0.0336	0.0406	20.52	0.3183	0.0641	0.1845	0.0026
S11	400m E	0.0968	0.1758	0.0126	0.0228	0.0298	0.0438	23.61	0.3037	0.0488	0.1921	0.0167
S12	450m E	0.0086	0.1991	0.0126	0.0278	0.0403	0.0621	34.01	0.2918	0.3464	0.3063	0.0173
S13	500m E	0.1397	0.2768	0.0195	0.0376	0.0373	0.0648	31.93	0.4598	1.1114	0.2776	0.0224
S14	550m E	0.4498	0.2799	0.0468	0.0395	0.04-38	0.081	39.46	0.4397	0.244	0.0573	0.0078
S15	600m E	0.0846	0.3583	0.0179	0.0394	0.0487	0.0898	41.23	0.9353	0.9265	0.4186	0.0855
S16	50m S	0.0267	0.2902	0.0029	0.018	0.0176	0.0216	9.574	0.1134	0.2894	0.4791	0.0743
S17	100m S	0.2261	0.4997	0.0163	0.006	0.0071	0.0103	5.253	0.0671	0.6755	0.1313	0.1522
S18	150m S	0.2161	0.4942	0.0174	0.0032	0.0077	0.0107	5.16	0.0661	0.0416	0.1345	0.1437
S19	200m S	0.4943	0.4229	0.0485	0.047	0.0655	0.1102	44.04	0.3339	0.3558	0.8272	0.1594
S20	250m S	0.2025	0.2333	0.0192	0.0168	0.0158	0.0221	14.76	0.1621	0.0604	0.2306	0.1006
S21	300m S	0.0415	0.3166	0.0093	0.0286	0.0372	0.0568	25.83	0.2712	0.2357	0.1667	0.1624
S22	350m S	0.3621	0.8927	0.0345	0.0178	0.0296	0.0447	23.95	0.3761	0.075	0.1581	0.0074
S23	400m S	0.2813	0.1855	0.0304	0.0345	0.0437	0.0634	31.74	0.2668	0.1682	0.4187	0.0484
S24	450m S	0.0053	0.2314	0.0107	0.029	0.0333	0.084	23.78	0.4423	0.2289	0.5904	0.0592
S25	50m W	0.6229	0.1656	0.05	0.014	0.0148	0.0158	11.7	0.0808	0.0017	0.0911	0.2402
S26	100m W	0.0006	0.0572	0.0009	0.0095	0.0069	0.0035	2.665	0.0333	0.1474	0.0743	0.1965
S27	150m W	0.003	0.1048	0.0045	0.009	0.0121	0.008	5.302	0.0716	0.1872	0.2197	0.1242
S28	200m W	0.0008	0.0606	0.0037	0.0098	0.0099	0.0053	2.892	0.0491	0.3846	0.0372	0.154

S29	250m W	0.0018	0.0557	0.0001	0.0109	0.0092	0.0042	2.942	0.04	0.7639	0.0456	0.1165
S30	300m W	0.0181	0.0662	0.0008	0.0062	0.0083	0.0049	2.233	0.0295	0.6136	0.1769	0.1831
S31	350m W	0.0026	0.0514	0.001	0.0124	0.0089	0.0143	1.993	0.0259	0.3868	0.0677	0.0586
S32	400m W	0.0021	0.0523	0.0013	0.011	0.0067	0.0026	2.11	0.0279	0.3336	0.2274	0.0931
S33	450m W	0.0012	0.0597	0.0017	0.0096	0.0095	0.0038	3.522	0.0382	0.7363	0.2669	0.1124
S34	500m w	0.0025	0.0686	0.0011	0.0098	0.0104	0.0042	3.466	0.0361	0.2142	0.4765	0.1945
S35	550m w	0.1597	0.1306	0.0147	0.0167	0.0257	0.0132	10.07	0.0894	1.163	0.1521	0.1297
S36	600m W	0.3411	0.1205	0.0275	0.014	0.0229	0.0105	8.804	0.0575	0.1917	0.0262	0.17
S37	650m W	0.0984	0.1205	0.0096	0.0156	0.0234	0.0087	8.34	0.0853	0.3323	0.106	0.1237
S38	700m W	0.0062	0.0824	0.0007	0.0119	0.0117	0.0053	4.528	0.0459	0.0516	0.053	0.167
S39	750m W	0.1565	0.1044	0.013	0.0114	0.0296	0.011	11	0.1065	0.6607	0.3516	0.1405
S40	800m W	0.0067	0.0931	0.0021	0.0101	0.0116	0.004	3.845	0.0406	0.2243	0.4118	0.1417
S41	850m W	0.0022	0.0907	0.0004	0.0113	0.0094	0.037	2.338	0.0395	0.3732	0.1517	0.1611
S42	900m W	0.0024	0.0643	0.0003	0.0094	0.0131	0.0039	3.24	0.037	0.2025	0.3768	0.1048
S43	950m W	0.0009	0.0665	0.0005	0.01	0.0118	0.0056	3.933	0.0314	0.4199	0.4715	0.133
S44	1000m W	0.0052	0.0878	0.0002	0.0117	0.0134	0.0061	5.538	0.0424	0.5035	0.121	0.1818
S45	1050m W	0.0038	0.0716	0.0006	0.0102	0.0104	0.006	3.319	0.0368	0.196	0.516	0.1392
S46	1100m W	0.0013	0.0683	0.0029	0.0093	0.0106	0.0044	3.499	0.0359	0.0769	0.073	0.1539
S47	1150m W	0	0.0766	0.0003	0.0095	0.0127	0.0057	4.887	0.0383	0.441	0.1619	0.1748
S48	1197.5m W	0	0.0425	0.0009	0.0078	0.0054	0.005	1.896	0.0255	0.192	0.1995	0.1559
Minimum	0		0.0425	0.0001	0.0032	0.0054	0.0026	1.74	0.0255	0.0017	0.0262	0.0012
Maximum	0.6229		0.8927	0.0676	0.0677	0.0807	0.1412	51.96	0.9353	1.163	0.8272	0.2677
Mean	0.112039		0.19714	0.01315	0.01835	0.02365	0.02914	14.0189	0.16609	0.31627	0.27839	0.1145

*: Direction and distance from the hot spring.

3.1.7. Petrographic Analysis

The geology of the study area comprises of the basaltic rocks of the Karoo lavas. However, outcrops of these rocks are rare in the area; they are covered by deposits of the Kalahari beds.

Five representative rock samples were collected from the patchy outcropped of the basaltic rocks in the vicinity of the hot spring for petrographic analysis.

In the hand specimen the basalt appears greenish grey with white and green amygdules. The white amygdules are more prevalent than the green amygdules.

In thin section the analyzed samples of the basalt show amygdaloidal texture with variable sizes of amygdules. The size of the amygdules varies up to 2 mm. The predominant white amygdules in the hand specimen turned out to be filled by zeolites with generally coarse grain size. In local places the vesicles are visible in the basalt and display variable sizes. This indicates that the basalt initially had a vesicular texture which resulted from high gas content released during the crystallization of the basalt.

The petrographic investigation shows that the basalt is essentially made up of fine lath-shaped plagioclase and fine anhedral clinopyroxene crystals associated with considerable amount of opaque minerals. The grain size of the plagioclase and pyroxenes are mostly less than 0.5 mm. The volume percentage of the plagioclase in the basalt is quite variable ranging between 70% and 45%. Moreover, the grain sizes of the plagioclase crystals are locally variable. In some samples the amount of clinopyroxene exceeds that of plagioclase. This indicates that the basalt has variable modal composition.

The modal content of the opaque minerals vary between 5 and 10%. Othopyroxene and amphibole occur in trace amounts.

3.2. Discussion

3.2.1. Physico-chemical Parameters

The spring and the groundwater from the pits north of the spring are slightly alkaline to alkaline, brackish to saline and hard to very hard whereas the groundwater west of the springs, river water and the sewage water are acidic to slightly alkaline (with the exception of sample W11, which is alkaline), fresh (with the exception of sample W12, which is brackish) and soft to hard.

The TDS value of the spring water and all the samples of groundwater from the pits north of the hot spring show a significant high value of TDS as compared to the groundwater samples from the west of the spring, the sewage and the river waters. This suggests that the hot spring is not from infiltration of local precipitation or fresh surface water. The source area is of regional rather than local extent.

With the exception of one groundwater samples (W5, 200m N of the spring), all the samples of the groundwater

from the pits north of the hot spring and the hot spring show a hardness greater than the alkalinity, signifying non-carbonate hardness. The water samples from sewage, river and all the groundwater samples from the pits west of the hot spring (with the exception of one groundwater samples from the west, W12), however, show a hardness less than the alkalinity; suggesting the hardness of these waters is carbonate hardness.

The non-carbonate hardness nature of the hot spring and all the groundwater north of the hot spring also revealed that the origin of the hot spring and the groundwater north of the hot spring is not local rather a result of deep water circulation from buried regional structures.

More or less similarities in the TDS and pH values and identical carbonate hardness nature between the river samples and the groundwater samples from the pits west of the hot spring suggest that the groundwater in the west of the hot spring have a source similar to the river, which is direct precipitations and/or fresh surface water from rainfall; and the groundwater is the percolation of either or both of these sources.

3.2.2. Rock-Water Interaction

During weathering and water circulation in rocks and soils, ions are leached out and dissolved in groundwater. The geological formations, water-rock interaction and relative mobility of ions are prime factors influencing the geochemistry of groundwater. The use of scattered plots for TDS vs $\text{Na}/(\text{Na} + \text{Ca})$ and TDS vs $\text{Cl}/(\text{Cl} + \text{HCO}_3)$ can help to identify rock-water interaction processes.

As shown in the figure 4, the hot spring, all the samples of the groundwater from the pits north of the hot spring and two samples (W11 and W12) of the groundwater from the pits west of hot spring lie in the region of evaporation – crystallization dominance whereas all the samples of the groundwater from the pits west of the hot springs (with the exception of sample W11 and W12) and the river water lies on the boundary of rock weathering dominance and atmospheric precipitation dominance signifying the role that both of them play in the chemistry of the groundwater west of the hot spring and the river water.

Figure 4 Gibbs diagram for cations and anions in (meq/l).

The impact of the rock weathering dominance to the chemistry of groundwater is dependent on the type of rock weathering processes that operate while the groundwater percolates through the different geological formations of the area: precipitation induced chemical weathering along with the dissolution of rock-forming minerals can modify the groundwater chemistry.

Figure 5 (Ca + Mg) versus (HCO₃ + SO₄) scatter diagram for the study area.

To differentiate the rock weathering processes that operate in the area under study the samples were plotted in the figure 5, Ca + Mg Vs HCO₃ + SO₄. As shown in the figure the hot spring, all the samples of the groundwater from the pits north of the hot spring and two groundwater samples from the pits west of the hot spring (W11 and W12) lie below equiline 1:1, indicating silicate weathering is the major weathering process that has influenced the chemistry of the groundwater

All the samples of the groundwater from the pits west of the hot spring, with the exception of W11 and W12, and the river water samples, however, fall along the equiline 1:1, indicating that samples have a balanced concentrations of Ca + Mg) and (HCO₃ + SO₄).

3.2.3. Cations, Anions and Trace Elements

From the analysis of the major ions in the water samples, it was observed that Ca²⁺ and Na⁺ are the dominant cations, with the exception of sample W12,

which is from west of the hot spring, where the concentration Mg²⁺ is greater than that of the concentration of Ca²⁺. In the hot spring and in all the analyzed samples north of the hot spring Na⁺ is the dominant cation followed by Ca²⁺ and Mg²⁺ whereas in all the samples west of the hot spring Ca²⁺ is the dominant cation followed by Na⁺ and Mg²⁺. In sample W12 Na⁺ is followed by Mg²⁺ and Ca²⁺. The concentrations of both K⁺ and Li⁺ in the hot spring and all the groundwater samples from the pits north of the hot spring are greater than the concentrations in all the other samples.

A Ca²⁺/Mg²⁺ molar ratio in water samples that is equal to one indicates dissolution of dolomite rocks, while a greater ratio may represent a more dominant calcite contribution from the rocks. A Ca²⁺/Mg²⁺ ratio, greater than 2 represents the dissolution of silicate minerals into the groundwater [8]. The hot spring sample and all the groundwater samples from the pits north of the hot spring have a Ca²⁺/Mg²⁺ ratio greater than 2, which indicated the dissolution of silicate minerals into the groundwater. The abundance of Ca²⁺ and Mg²⁺ in the hot spring and all the groundwater samples from the pits north of the hot spring could be related to the presence of basaltic rocks in the area in which silicate minerals are the dominant minerals in the rocks. Weathering of these minerals might have contributed Ca²⁺ and Mg²⁺ to the spring and groundwater (Eq 2 to 4). The thin section study of the rocks from the studied area indicated that plagioclase and pyroxenes are the two dominant minerals in the rock. The weathering of plagioclase, pyroxene and biotite minerals could be represented in the following reactions; equations (2) to (4) in natural systems:

With the exception of two samples, all the groundwater samples from the pits west of the hot spring had a Ca²⁺/Mg²⁺ ratio between 1 and 2, which indicated that the dissolution of calcite. One of the groundwater samples from the pits west of the hot spring had a Ca²⁺/Mg²⁺ ratio higher than 2 indicating the dissolution of silicate minerals. This sample is the one nearest to the hot spring as compared to the others. The other groundwater sample from the pits west of the hot spring had a Ca²⁺/Mg²⁺ ratio

less than one. The river sample reflects the same value to that of the groundwater samples from the pits west of the hot spring

With the exception of one sample, $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio values of groundwater samples from the pits west of the hot spring are slightly higher than river water; suggesting that the groundwater is recent and does not have long residence time within the rocks of the area. This slight increment of $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio values in the groundwater is due to more dominant calcium contribution from the dissolution of plagioclase minerals in the rocks of the study area as it was explained above in the form of reaction (Eq 2).

The trend of concentrations of Na^+ and K^+ ions in all the analyzed samples are different from that of Ca^{2+} and Mg^{2+} . In the hot springs and in all the samples of the groundwater from the pits north of the hot spring the concentrations of Na^+ and K^+ ions are much higher than the concentration of Ca^{2+} and Mg^{2+} ions: suggesting that the dissolution of plagioclase and pyroxene minerals is not the only source of these elevated values of Na^+ and K^+ ions in these water. In all the samples of groundwater from the pits west of the hot spring and river water, the concentrations of Na^+ and K^+ ions show the same trend to that of the concentrations of Ca^{2+} and Mg^{2+} in these water. The elevated concentrations of Na^+ and K^+ ions in the hot springs and in all the samples of the groundwater from the pits north of the hot spring signifying more supplements of the deep fluids that have deep origin.

The general dominance of anions in the hot spring and all the groundwater samples from the pits north of the hot spring were in the order of $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{Br}^- > \text{F}^- > \text{CO}_3^{2-} > \text{NO}_3^-$. In all the samples west of the hot springs and the river water the dominant anion is bicarbonates with chloride being subdominant, followed by sulphate: $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{PO}_4^{3-} > \text{NO}_3^- > \text{F}^- > \text{Br}^- > \text{NO}_2^-$. This is with an exception to two samples (sample W11 and W12). In the two samples sulphate is the dominant anion with chloride being subdominant, followed by bicarbonate: $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^- > \text{CO}_3^{2-} > \text{NO}_3^- > \text{Br}^- > \text{F}^-$.

Cl^- and SO_4^{2-} are not the major constituents in the minerals of basaltic rocks. The dominance of Cl^- and SO_4^{2-} in the hot spring and in all the samples of the groundwater from the pits north of the hot spring suggesting more supplements of the deep fluids that have deep origin.

With exception of sewage water, PO_4^{3-} is absent in all the analysed water samples. In sewage water its concentration reaches up to 88.1 mg/l. NO_2^- are absent in the hot spring, in all the groundwater samples from the pits north of the hot springs, in the river water sample and in sewage samples. In the samples of the groundwater from the pits west of the hot spring NO_2^- exist only in the samples W6, W7, W9, W10 and W13 only having minor concentration. In the remaining samples is NO_2^- absent. With the exception of one of the sewage sample ($\text{NO}_3^- = 20.23 \text{ mg/l}$), NO_3^- is found having a minor concentration in

all the analyzed water samples. The high concentrations of PO_4^{3-} and NO_3^- in the sewage water are mainly attributed to sewage effluents. Nitrogen compounds (ammonium salts, nitrites and nitrates, etc.) found in urban water bodies are mainly due to decomposition of proteinous compounds which enter with sewage. In the hot spring and in all the samples of groundwater from the pits north of the hot spring bromide was detected having a significant concentration whereas in all the samples of groundwater from the pits west of the hot spring, river samples and sewage samples the concentrations of bromide is minor. The existence of bromide having such concentrations in the hot spring and in all the samples of the groundwater from pits north of the hot spring is attributed to the supplements of the deep fluids that have deep origin.

The analyzed cations and anions in both sediments and water samples more or less show the same trend of dominance but vary in magnitude of concentration. In the sediments samples the dominant cations are Na^+ , Ca^{2+} and K^+ and the dominant anions are Cl^- and SO_4^{2-} . Such compositional nature of the sediments suggests that the source of the cations and anions for the water is not linked to the composition of the sediments rather to the different processes and origin describe above.

The analyzed trace elements in both the sediments and water samples more or less exhibit the same trend of dominance but vary in magnitude of concentrations. The concentration of each analyzed trace element is greater in sediment than in the water with the exception of the concentration of Ni: the concentration of Ni in the water samples is greater than the concentration of Ni in the sediments.

The concentration of Ni is high in the hot spring and the groundwater from the pits north of the hot spring followed by the sewage water and then the groundwater samples from the pits west of the hot spring and the river samples.

The abundance of Ni in igneous rocks generally correlates with those of Mg, Cr and Co. Even though the bed rocks are basaltic rocks, this general truth is not applicable in the case of the study area. Ni concentration is much higher than the concentration of Cr and Co. The mean concentration of Ni in the hot spring and the groundwater samples from the pits north of the hot spring is 1.754 mg/l. The mean concentration of Ni for the groundwater samples from the pits west of the hot springs and river water sample is 0.529 mg/l whereas from the sewage samples the mean is 0.795 mg/l. The high concentration of Ni in the groundwater west of the hot springs, river water and sewage is both by silicate weathering, sewage itself and leachate from the waste. The high concentration of Ni in the hot spring and in the groundwater from the hot spring is related deep seated origin of the fluid or magmatic fluids.

All the remaining analyzed trace elements in the groundwater from pits west of the hot springs, sewage and

river could be derived from precipitation dissolution of minerals. Generally, the analysed trace elements in the hot spring and in the groundwater samples from the pits north of the hot spring have origin from fluids of deep origin.

All the analyzed trace elements, in the sediments from samples west, east, south of the hot spring are could be derived from silicate weathering. The iron (Fe) concentration in the sediment is much higher than its concentration in the water samples. Since clay minerals carry more iron than sand grains, this element is principally associated with silt-clay fraction.

3.2.4. Water Suitability

The analyzed cations, anions and trace elements of the hot spring water and all the samples of groundwater from the pits north and west of the hot spring are compared and evaluated with respect to the drinking water standards set by Botswana Bureau of Standards (BOBS) [9] and World Health Organisation (WHO) [10] (table 6).

Table 6. Drinking water standards by WHO and BOBS.

	BOBS	WHO
EC ($\mu\text{S}/\text{cm}$)	1500-3100	1500
pH	5-10	6.5-9.5
TDS (mg/l)	1000-2000	
Ca (mg/l)	150-200	
K (mg/l)	50-100	
Na (mg/l)	200-400	200
Mg (mg/l)	70-100	
Cl (mg/l)	200-600	250
F (mg/l)	1-1.5	1.5
NO_3 (mg/l)	50	50
NO_2 (mg/l)	3	3
SO_4^{2-} (mg/l)	250-400	500
Zn (mg/l)	5-10	
As (mg/l)	0.01	0.01
Cd (mg/l)	0.003	0.003
Cr (mg/l)	0.05	0.05
Co (mg/l)	0.5-1	
Cu (mg/l)	2	2
Fe (mg/l)	0.3-2	
Pb (mg/l)	0.01	0.01
Mn (mg/l)	0.1-0.5	0.4
Ni (mg/l)	0.07	0.02
Ba (mg/l)	0.7	0.7

The hot spring, all the samples of groundwater from the pits north and west of the hot spring satisfy the pH drinking water standard of both WHO and Botswana Bureau of Standards.

With the exception of the sample W12, all the samples of groundwater from pits west of the hot spring suit the EC and TDS standard of both WHO and Botswana Bureau of Standards whereas sample W12, hot spring water and all the samples of groundwater from the pits north of the hot

spring is highly above the recommended limits of standards set by both WHO and Botswana Bureau of Standards.

All analysed cations and anions in all the samples of groundwater from pits west of the hot spring, except sample W12, satisfy the standard of both WHO and Botswana Bureau of Standards Because of the existing concentration of Na^+ , Cl^- , Br^- and SO_4^{2-} , sample W12, hot spring water and all the samples of groundwater from the pits north of the hot spring do not satisfy the standard of both WHO and Botswana Bureau of Standards.

The analysed hot spring water and all the samples of groundwater from the pits north and west of the hot spring don't satisfy the standard of both WHOM and Botswana Bureau of Standards because of the existing concentration of Ni and Pb in the waters.

4. Conclusions

The hydrogeochemistry of any source of water is an important aspect of knowledge in order to address matters such as contamination and quality. In the analyzed water samples generally based on the mean values of the chemical parameters, the cations were in the order of abundance as $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Li}^+$ and the anions were in the order of abundance as $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{PO}_4^{3-} > \text{Br}^- > \text{CO}_3^{2-} > \text{NO}_3^- > \text{F}^- > \text{NO}_2^-$. In the analysed sediment samples the cations and anions are in the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+} > \text{Li}^+$ and $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^- > \text{Br}^- > \text{NO}_2^- > \text{PO}_4^{3-}$, respectively. 75 % the analyzed groundwater samples from the pits west of the hot spring show some similarities in the trend of concentration of the different constituents of the groundwater with the river water, suggesting that the groundwater is recent or derived from precipitation. A slight increment of values in the analyzed major cations, anions, and trace elements in the groundwater of this area is due to the dissolution of different minerals in the rocks of the study area. The remaining 25% the groundwater samples from this part of the study area suggest that precipitation is not the sole source of groundwater and it could be derived from both precipitation and fluids of deep origin.

The hot spring and the groundwater north of the hot springs are characterized by higher mineralization, and this could be attributed to the more supplement of the deep fluids that have deep origin. This implies that the source of the spring and the groundwater north of the hot spring have a regional origin.

The hot spring water and all groundwater in the studied area are not recommended for drinking purposes.

Acknowledgements

The authors duly acknowledge Office of Research and Development of University of Botswana for sponsoring this research work.

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