Hydrochemical evaluation using statistical analysis for the deeper Nubian aquifer in Tazerbo Wellfield area, southeastern Libya.

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Abstract

The chemical parameters of groundwater play a significant role in classifying and assessing water quality. The Statistical analyses of this paper relied on previously collected data from Great Man-Made River (GMRA), in terms groundwater chemistry and hydrogeological

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characteristics of the Tazerbo aquifers. Understanding the chemical compounds and to know the sources of pollution in the groundwater to preserve water resources until other water resources are discovered become very important. Statistical analysis method and Principal Component Analysis (PCA) was applied to summarize the results of chemical analysis in terms of maximum, minimum, and mean values. Subsequently, the samples were analyzed in the laboratory for their chemical constituents using standard methods. According to results, the Nubian aquifer over the Tazerbo wellfield dominant with two main water facies are namely alkali carbonate facies and mixed types facies, the water source for these water according to Gibbs boomerang is evaporation, also Tazerbo wellfield water have an excellent to good water classes classification according to salinity hazard ratio. However, this result can be seen from the low value of chloride ions as indirect indication of low salinity of the groundwater.

The dissolved oxygen used to indicate the potential of Tazerbo wellfield water to cause corrosion or to precipitate incrustating deposits on wells pumps and pipelines, also increasing in potassium rates, is a function of temperature since higher dissolution rates occurring at higher temperatures. Three main PCA groups were defined for the Nubian aquifer within Tazerbo wellfield, reflecting the dominance of an exogenetic elements, changing in water temperature due to increasing of potassium concentration and influenced by geological formations during water formation.

1. General:

Large-scale development of groundwater has caused decreases in the amount of groundwater that was present in coastal aquifer storage and that pumped to the coastal cities. The water supply in coastal cities, was not adequate to meet demand, and severe drought is affecting large parts of Libya. Nowadays in Libya water demand is projected to heighten the current stress on groundwater. The chemical parameters of groundwater play a significant role in classifying and assessing water quality. The development of groundwater resources in these arid and semi-arid regions is a sensitive issue, and careful management is required to avoid water-quality degradation (Dassi 2010; Trabelsi et al, 2007). Variation of groundwater quality in an area is a function of physical and chemical parameters that are greatly influenced by geological formations and anthropogenic activities (Belkhiri et al. 2010). This study area represents a typical multi-layered aquifer system that is mostly under some confined conditions.

Hydrogeochemical processes affecting the groundwater chemistry of an area using ionic relationships and groundwater facies analysis have been carried out by many workers (Alaya et al. 2014; Varol and Davraz 2014; Chaudhuri and Ale 2014). Multivariate statistical analysis, mainly Principal Component Analysis (PCA), has been used effectively across many regions of the world to identify the various geological and anthropogenic factors that affect the groundwater chemistry of an area (Galazoulas and Petalas 2014; Salman et al. 2014; Parizi and Samani 2013). The present work aimed to understand the spatial distribution of hydrochemical constituents of Tazerbo wellfield groundwater related to grouping in chemical elements concentration, determining water facies, detecting water source and delineating the water salinity hazard.

2. Location:

The target zone located within the southeastern portion of Libya and it is also a part of the Nubian aquifer (Figure 1). It is found in a flat desert zone at the southern restrain of the Sarir Plain and covers an area of 1000Km^2. The Tazerbo Wellfield lies along the southwest northeast arrangement of the southern flank of the Hercynian uplift which shapes a boundary that isolating Kufra basin from Sirt basin. The Wellfield comprises 108 high pumping capacity water well at 100 l/s of each well and encompassing twenty-one piezometers for checking the inactive water level and for estimation of the transmissivity and storage coefficient over the Wellfield.

3. Geological and Hydrogeological Setting:

Tazerbo wellfield referring to it is stratigraphic succession attributed to part of the Kufrah basin comprises thick suite of mainly siliciclastic rocks were deposited form from Cambrian to Cretaceous time (Figure 2). Structurally, Al Kufrah Basin is characterized by Caledonian and Hercynian structural elements generated during polyphase deformation. It is separated from the Murzuq Basin (to the west) and from the Sirt Basin (to the north) by the NNE–SSW- trending Tibesti-Sirt Arch and the Tazerbo-Az Zalmah Arch, respectively, which were uplifted during the Hercynian orogeny and which lack post-Hercynian sedimentary cover (e.g., Bellini and Massa, 1980; Hallett, 2002). To the east, the Al Kufrah Basin is structurally limited by the Hercynian Ennedi-Oweinat Uplift; the NNE–SSW elongation of the Al Kufrah Basin generally coincides with the Hercynian Borkou-Al Kufrah Trough (Bellini and Massa, 1980).

Three aquifers have been recognized within the south indicated as shallow, medium, and deep aquifers with moderately uniform and broad layering and isolated by thick aquitards lying above and beneath the main aquifer consist of shale, and fine grained argillaceous, ferruginous sandstones with mudstone interbeds (Pim and Binsariti 1994). The deep/main aquifer is the target of The Great Man-Made River (GMRA). It is truncated within the north by clays and could be a 100-120m thick horizon of well-sorted, medium-grained, poorly cemented sands, which are formed at 280m profundity within the north-west and 500m profundity within the southeast of the southern aquifer (Tazerbo and Al Kufra). The aquifer plunges at an angle of 2-3^{o} to the southeast, the water appearance is variable from one location to another, from 260m within the northeast and northwest to 400 m within the southeast and southwest.

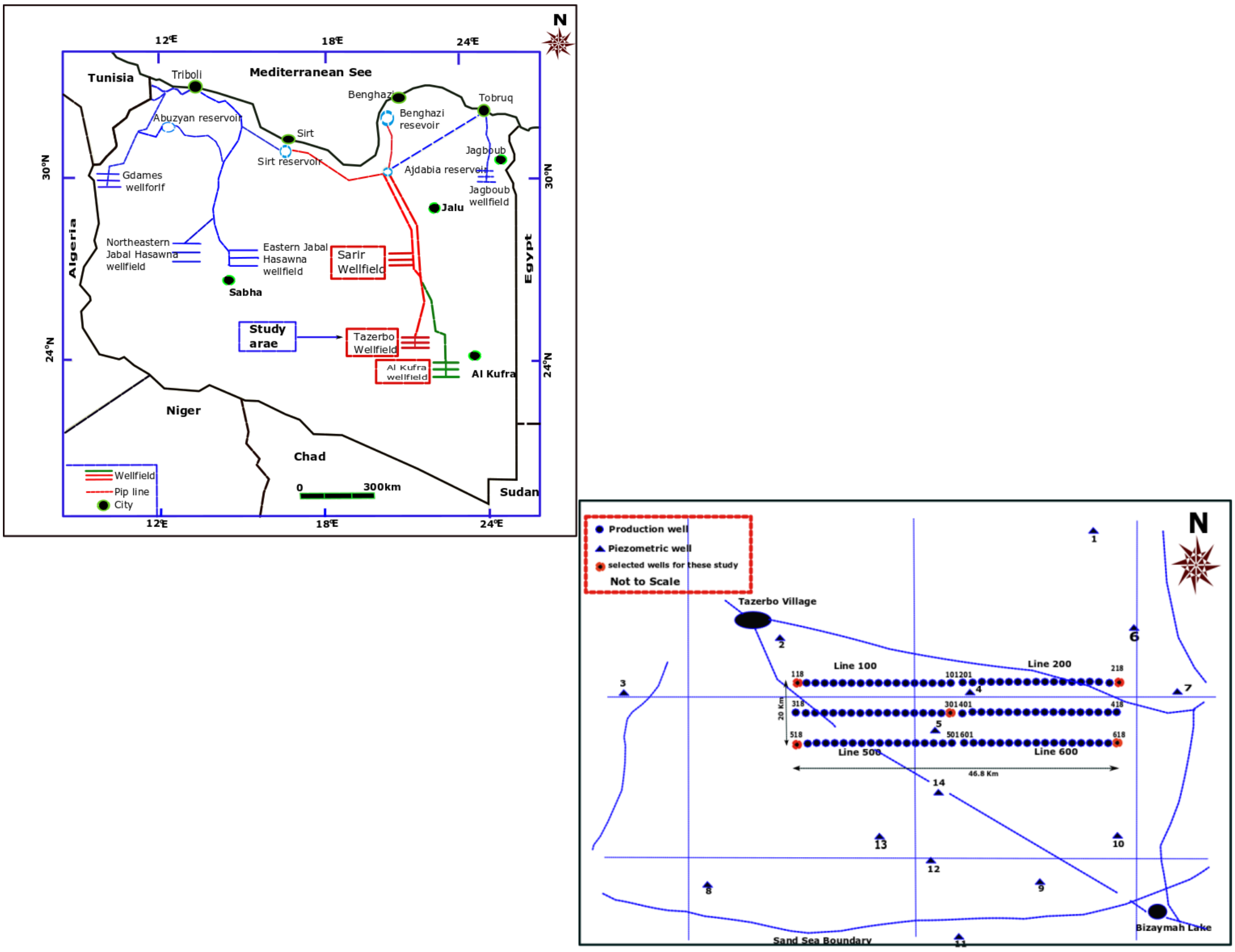

Figure 1: (A) is general map of Libya shows the main water wellfields including Tazerbo wellfeild location (the study area), and main water reservoirs (Mostafa, 2019), (b) distribution of pumping and piezometers wells in the study area the (modified after Al Faitouri, 2013).

This work surveys and evaluate the physical and chemical parameters of groundwater from 55 diverse wells are locating over the wellfield in wide different zones. The strategies utilized for this ponder are field estimations, testing, and research facility investigation were made by a set of 93 groundwater samples were analyzed for 17 physical and chemical parameters comprising major elements concentrations, electrical conductivity (EC), and (pH) after pumping for ten minutes to expel out water within the wells. Each test for every single sample was immediately filtered using 0.45L filters of acetate cellulose and was transferred into 0.1L polyethylene bottles.

Immediately inspecting, temperature, pH, and electrical conductivity (EC) were measured within the field by employing a multi-parameters WTW, P3 Multi-Line series pH and LF-SET. Hence, the tests were analyzed within the research facility of MRA for their chemical utilizing standard strategies as proposed by the American Public Health Association (APHA 1989, 1995a, 1995b).

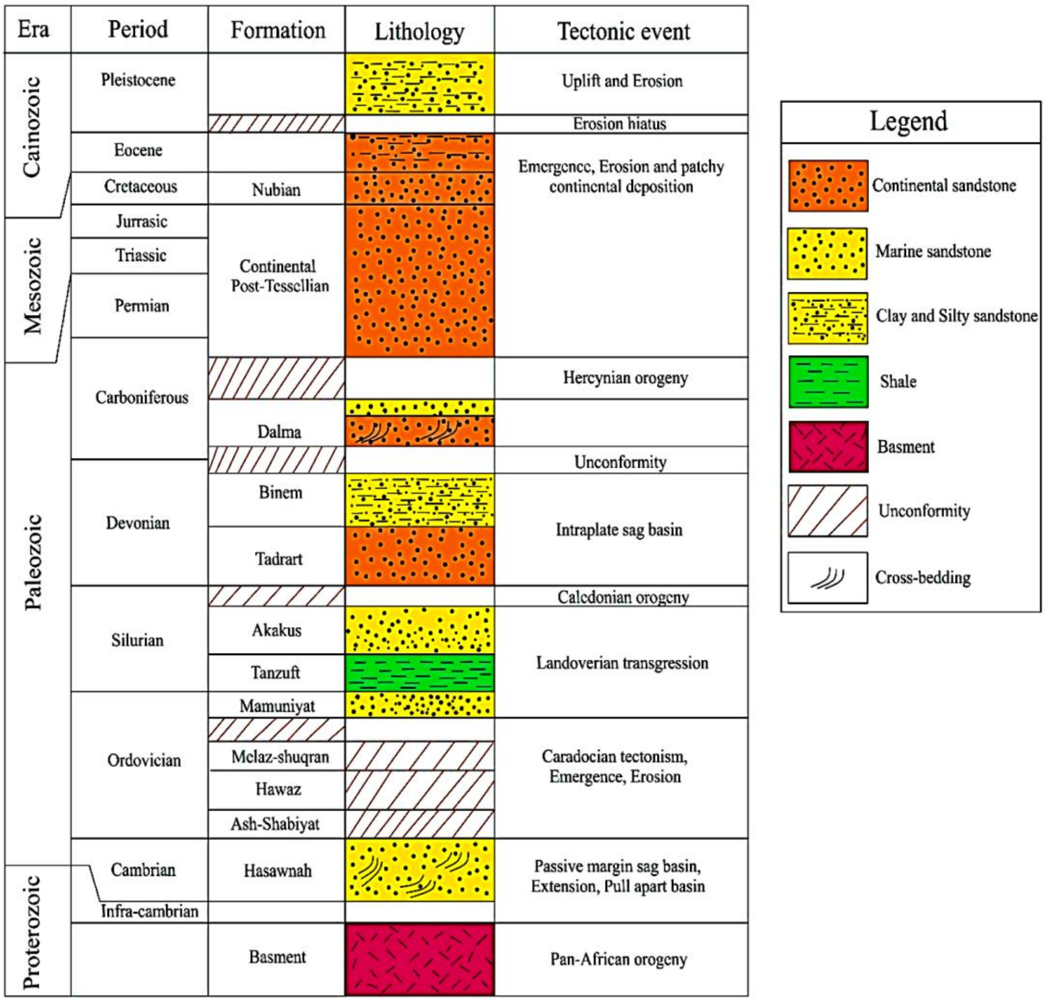

Figure 2: general lithostratigraphic columnar section defined formations of Al Kufra basin and relating to tectonic events over the basin. Modified after (Hallet, 2002), (Hallet, 2016), and (Al Farrah et al, 2017).

3.1. Statistical and Investigation Methods:

Multivariate statistical analytical methods were also used in this study to effectively interpret data in groundwater, the physical and chemical parameters were calculated in terms of maximum, minimum and mean average, this part aiming to restrict the data with an adequate average for interpretation. Principal Components Analysis (PCA) is useful in reducing data dimension while retaining important information and representing variables in a form that can be easily interpreted (Singh *et al.* 2005). The statistical software package XL STAT 2017 for windows was used for the multivariate statistical calculations. The statistical analysis of PCA were carried out by the classification and data reduction modules, respectively.

The investigation methods followed for water facies such Piper plot, water source determination Gibes boomerang and determining the salinity hazard Wilcox graph were extracted using different softwares namely Rock Work 16 and Origin Lab 2018.

4. Results and discussion:

4.1. Hydrochemical evaluation:

According to results (Table 1 and Table 2) that summarize the geohydrochemical data in terms of maximum, minimum and mean, the overall mean water temperature of Tazerbo Wellfield is 32.31^{o}C, with a minimum value of 27.2 ^{o}C and a maximum value is 35.5 ^{o}C, Temperature changes may also have an impact on the redox chemistry of groundwater. For example, in a set of column experiments warming from 10 to 70 °C resulted in a shift of the observed redox conditions as the biogeochemical conditions changed from oxic respiration to iron and sulfate reduction (Jesußek et al., 2013). The pH balance of a water supply describes how acidic or alkaline is it), recognizable variation was also observed in the pH values of Tazerbo Wellfield water. Thus the overall average pH value was 8.039, whereas a minimum value of 7.71 and a maximum value of 8.3, according to (Tikhomirov, 2016) these results suggesting water is weak alkalinity water.

Tazerbo Wellfield in general has high concentrations of dissolved oxygen, with averages as 7.73mg/l when oxygen concentrations are less than 2mg/L, the water is defined as hypoxic, but in this case these high concentration of oxygen in water may causes corrosion, which facilitates destruction of materials of engineering facilities. The concentration of CO_2 is low and reported in most wells indicating low carbon water.

Table 1: Statistical data in terms of maximum, minimum and mean for the site measurements and general parameters, the fundamental units were labeled for every single parameter.

Statistical Parameter	Temp °C	pH	CO_2 mg/l	Turbidity FNU	EC µS/cm	ORP mv	D.O. mg/l
Max	33.3	8.3	1	1.48	287	377	8.67
Min	28.7	7.71	0	0.04	238	158	6.44
Mean	31.2771	8.039	0.39	0.2313186	266.42391	280.05	7.73554

The US Salinity Laboratory (1954) classified ground waters on the basis of electrical conductivity. The water overall EC mean value was 266.4 µS/cm, reflecting good EC values for this Nubian water certainly reflect the relatively low dissolved solids content of the water. The average value of the total dissolved solids concentration in groundwater for any purposes should be below 500 mg/l (Catroll 1962; Freeze and Cherry 1979), However Tazerbo Wellfield TDS is 280.61 mg/l, based on Freeze and Cherry (1979), all groundwater samples collected from Nubian deep aquifer are fresh in nature, also water is characterized by reducing conditions with almost all wells having a negative oxidation-reduction potential (ORP).

Calcium average value was 9.50 mg/l, reflecting an approximately homogenous distribution of calcium concentrations over the wellfield. Sodium cations concentrations showed some variation throughout Tazerbo Wellfield. The overall average, was found to be 11.39 mg/l while the concentrations of potassium cations were found to be greater than that of sodium cations in Tazerbo Wellfield with a mean value 27.2 mg/l.

Table 2: Statistical analysis for the chemical measurements for the Tazerbo wellfield water their (concentration in milligram per liter.)

Statistical Parameter	Ca mg/l	NO_3 mg/l	Na mg/l	K mg/l	CCPP mg/l	Mn mg/l	Cl mg/l	SO_4 mg/l	Mn mg/l	Total Hard. as CaCO3
Max	13.8	0	13.79	36.83	-0.1	0.065	31.95	12.3	0.065	88.4
Min	1.95	0	7.1	19.4	-7	0	10.63	5.64	0	67.9
Mean	9.50	0	11.39	27.12	-3.10	0.0132	15.31	9.33	0.01	75.96

This situation seems to be reverse than most normal water, where sodium tends to be higher than potassium concentrations, rising of potassium levels are resulted from the chemical decomposition of the silica content especially clay minerals (Saha et.al, 2019). The chloride concentrations in The Wellfield water are moderately low and averaging at only 15.31 mg/l for the entire wellfield. The low value of chloride ions is an indication of low salinity of the groundwater of the study area. Nitrate was found to be 0.0 mg/l for all wells.

The occurrence of sulfate in groundwater resulted from the oxidation of sulfur of the igneous rocks, the dissolution of the other sulfur bearing minerals (Saha et.al, 2019). Sedimentary rocks, such as organic shale, may play a key role in this connection by the oxidation of marcasite and pyrite (Matthess 1982). The sulfate overall concentration in the wellfeild is 9.33 mg/l.

4.2. Water type:

Piper (1944) introduced a plot diagram which has been widely applied in hydrochemistry studies to find out the groundwater facies. The Piper plot was performed here by using Rock Work 16 software for this study is (Figure 2), indicates that the Nubian aquifer of the Tazerbo wellfield dominant with two main water facies, the first facies is alkali carbonate facies can be related to carbonate-rich minerals in aquifers. On the other hand, the second facies is mixed type facies. These differences can be explained by a mixing effect of the groundwater as it moves within the aquifer.

By moving to anions and cations concentrations the results showing dominant concertation for the Alkali carbonate and water cation suggesting sodium dominance, however water facies according to these results are mainly influenced by ion exchange, evaporation, and concentration (Huo et. al, 2016).

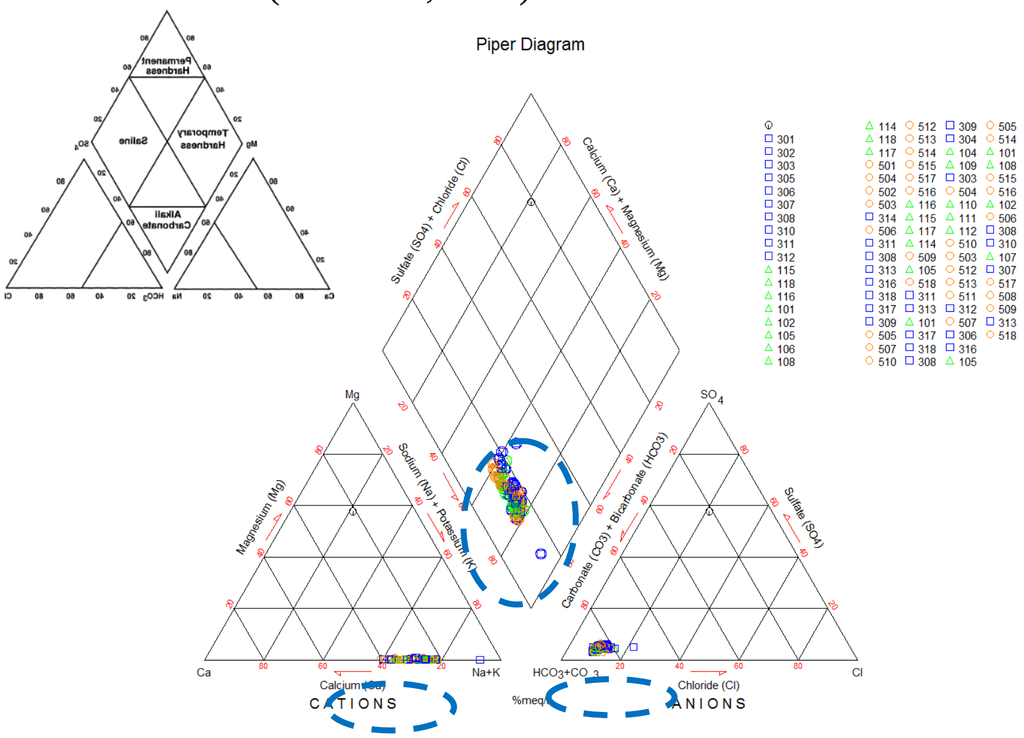

Figure 3: Piper (1994) plot for the Tazerbo wellfield water showing to main water facies identification.

Gibbs (1970), modelled boomerang does not reflect the influences of human activities on hydrochemical components, it is widely used within the analysis of natural, for defining water formation source. The Gibbs model map contains three areas representing the three important processes mechanisms responsible for hydrochemical elements of water, these areas namely precipitation, evaporation and rock weathering, it is widely used within the analysis of natural processes driving hydrochemistry in water (Li et al. 2016).

Boomerang plot (Figure 4), is also places the water within aquifer fill in the region of evaporation, indicating that water precipitation evaporation is a primary factor controlling the water composition, (Singh et al. 2005). According to (Kuwairi 2006) evaporation rates are high in the southern region of Libya up to 6,000 mm/year. None of the data plots lies within the lower side of Gibbs boomerang, where water composition is dominated by atmospheric precipitation process. These results confirm Al Faitouri and Sanford (2015), who concluded that no recent recharge for Tazerbo aquifer.

Wilcox (1955), used the sodium percentage and specific conductance in the groundwater in evaluating its suitability for irrigation. Sodium percentage determines the ratio of sodium concentration to the concentration of the total cations (sodium, potassium, and calcium). The values of sodium in percentage and electrical conductivity shows low values for both parameters (Figure 5), therefore an excellent to good water classes classification, Groundwater that fall within the C1-S1 and C2-S1 can be used for irrigation on all types of soil with little danger of the development of harmful levels of exchangeable sodium (Salifu et.al, 2015).

4.3. Principal component analysis (PCA):

Principal component analysis (PCA) is one such technique that extracts linear relationships existing among a set of variables, the more advanced methods of principal component analysis (PCA) for delineating the factors have influence for controlling the groundwater chemistry and to understand the spatial distribution of different major concentration in the groundwater, three main PCA groups were defined for the Nubian aquifer within Tazerbo wellfield (Figure 6).

The first group PC-1 showing a dominance with an exogenetic elements Mn, SO_4 and Mg, these group can be classified as source of anthropogenic activities, by moving to the second group PC-2 this group classify as K- TDS group that reflecting a source of fresh water and changing in water temperature due to increasing of potassium concentration. The last group PC-3 is Cl, Ca and Na group, these elements dominance reflecting the influenced by geological formations in water formation of water, these groups confirming the previous results and hydrochemical plots, for defining water formation mechanisms, in addition PCA results shows that the group PC-1 which influenced by some contaminant sources must be treated according to suitable guideline such as World Health Organization guidelines.

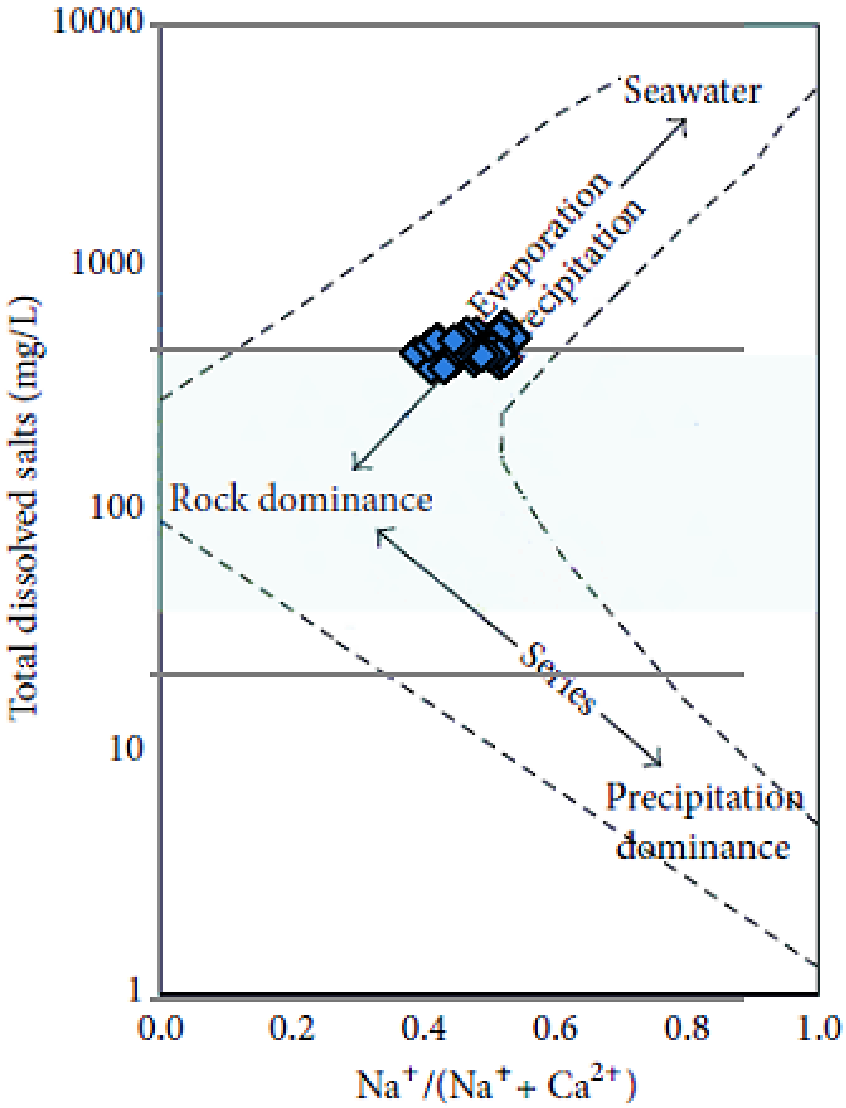

Figure 4: A semi-logarithmic plot modified according Gibbs boomerang (1970) for dqelineating water source formation.

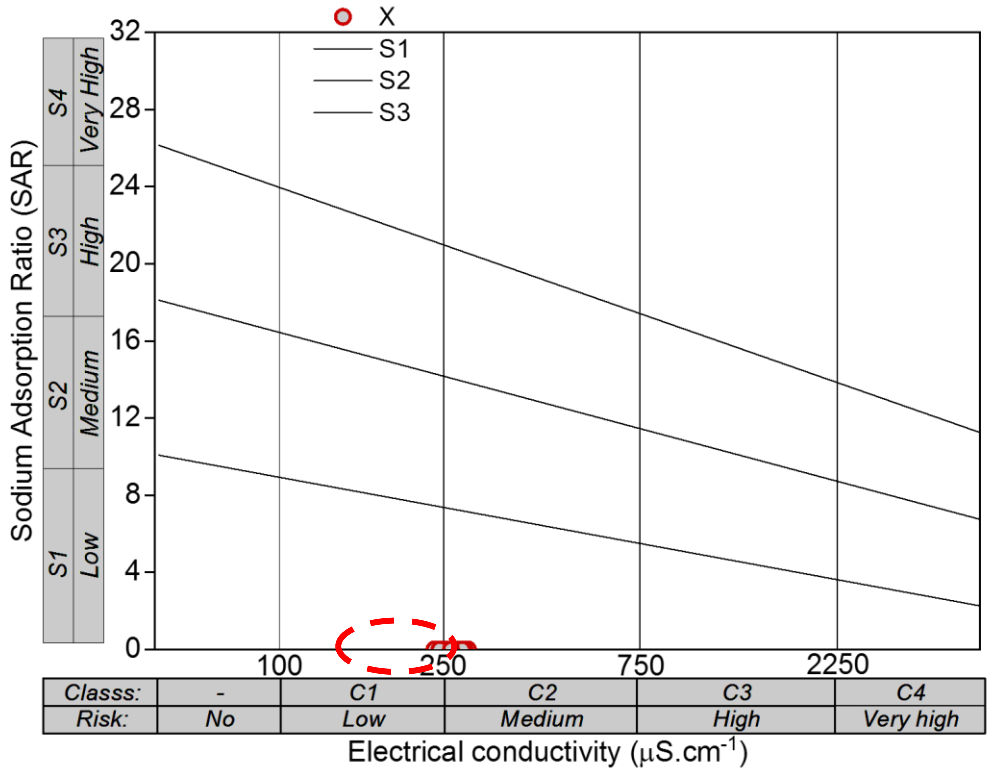

Figure 5: Wilcox (1955) plot for the sodium percentage and electrical conductivity, the main uses for groundwater evaluating and suitability for irrigation.

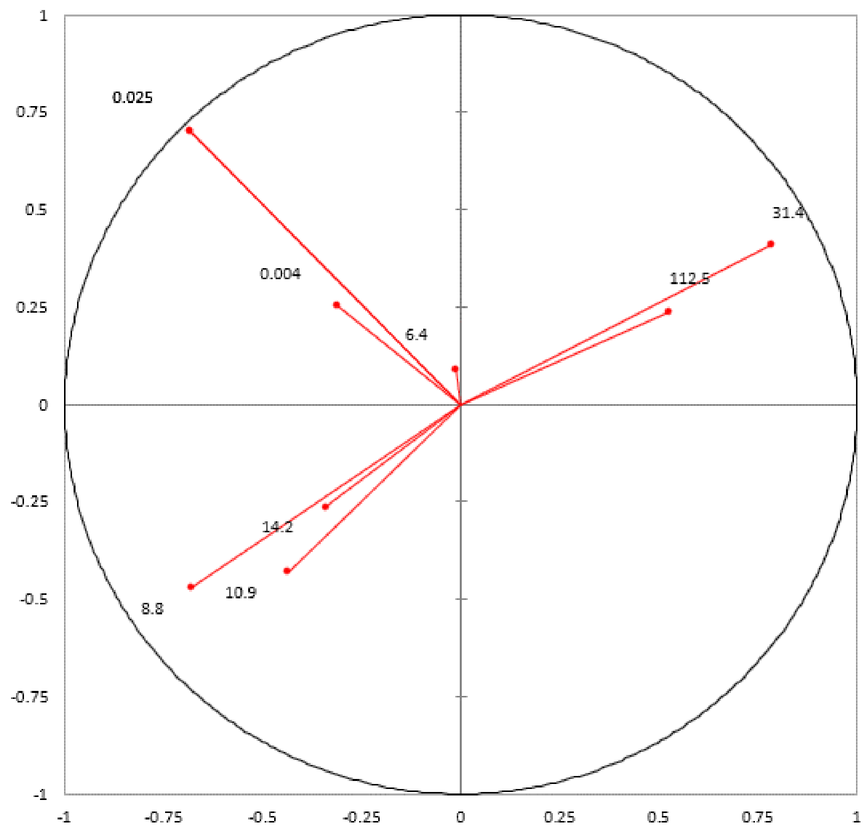

Figure 6: Principal Component Analysis (PCA) for delineating the factors for controlling the groundwater chemistry and to understand the spatial distribution of different major concentration in the groundwater.

5. Conclusions:

The Nubian aquifer in the Tazerbo wellfield dominated with two main water facies the alkali carbonate facies and the mixed types facies as result of mixing effect of the groundwater while it moves within the aquifer, the water source according to Gibbs boomerang is evaporation, this result confirm the previous isotopes studies for the water recharging source. Tazerbo wellfield water have an excellent to good water classes classification according salinity hazard ratio. However, this result can be indicated from the low value of chloride ions as indirect indication of low salinity of the groundwater. The determination of dissolved oxygen indicating the potential of Tazerbo wellfield water may cause corrosion or precipitate incrustating deposits on wells pumps and pipelines, therefore Increasing in potassium rates is a function of temperature rise since higher dissolution rates occurring at higher temperatures.

Three main PCA groups were defined for the Nubian aquifer within Tazerbo wellfield, the PC-1 group showing a dominance with an exogenetic elements, while PC-2 group reflecting a source of fresh water and changing in water temperature due to increasing of potassium concentration, and PC-3group reflecting the influenced by geological formations during water formation.

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