HYDROGEOCHEMISTRY AND GROUNDWATER QUALITY ASSESSMENT IN AZINTAN, NORTHWESTERN LIBYA

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Abstract - The groundwater aquifers in Azintan, northwestern Libya suffer from an acute shortage of water. The groundwater was evaluated to determine its suitability for drinking and irrigation purposes from major two aquifers in north and south of Azintan area. This study carried out to assess the groundwater quality and to identify major affecting variables. Twelve samples from the two aquifers were collected. The two aquifers were collected and analyzed for total dissolved solid (TDS), electrical conductivity (EC), pH, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, CO_3^{2-} and $HCO3^-$. The results show that, the groundwater in many places is dominated by higher concentrations of Cl^-, SO_4^{2-} and $HCO3^-$. Two water types were recognized in this region are Cl-SO4-Na-Ca and Cl-SO4-Na. Gibbs and Piper method, as well as the hardness, soluble sodium percentage and the permeability index all have been used to assess the diagram quality of the groundwater of aquifers. Further, the multiple correlations and Cluster Analysis of groundwater quality parameters were carried out for further classification and interpretation of the groundwater quality. Finally, water qualities in the study area are compared with Libyan standards and WHO guidelines of drinking water and irrigation purposes.

Keywords: (Cluster Analysis, Groundwater quality, hydrogeochemistry, Irrigation, Zintan).

I. INTRODUCTION

Libya's area of 1,750,00sq km is mostly desert. Only about 4 percent of Libya's area has both sufficient rainfall and adequate soil to be considerable. Most agricultural and other human use of water are dependent on groundwater. Only two regions of the country, the Jifarah-Jabal Nafusah region (study area) and Al Jabal Al Akhdar region, receive sufficient amount of rainfall in most years to provide significant recharge to groundwater. The area investigated

was the subject of numerous geological studies carried out by different geologists [19]; [8]; [12]; [24] The suitability of irrigation water depends upon many factors including the quality of water, soil type, salt tolerance characteristics of plants, climate and drainage characteristics of soil [10]; [16]. This study focused on the quality of water resources in an area that suffers from a severe shortage of water sources. The groundwater is the only source of water supply for most of the local demand (agricultural, industry, and domestic), as well as drinking and irrigation purposes. Azintan depends heavily on groundwater, which accounts for more than 97% of the water used (83% of agricultural holdings and 14% of household). There are no available water supply systems in the area. The only source for recharging groundwater aquifers is rainwater, which falls only in the winter season in December and January in limited quantities. Precipitation has an average annual rainfall of 150 mm per year. Libya has no rivers, and its surface run-off is limited to short floods following extreme rainstorms in the winter. This puts the total contribution of surface water at less than 3% of the existing water in use. Renewable basins are found in the north (Jifarah Plain, Jabal al-Akhdar and part of Hamada al-Hamra), while the other sedimentary basins (Murzuk, Kufra and Sarir) containing non-renewable groundwater. Renewable groundwater is estimated to be 600-650 MCM/yr. [7]. Other places that have local recharge because of rare heavy rain producing run-off have been observed in the Haruj Mountains in the centre of the country, at the Tibesti Mountains in the south and the Aweinat Mountains in the west. The recharge amount in these areas is minor and has little value compared to the storage values and aquifer losses [9]. Surface water in Jifarah plain, 170 MCM/yr. collected from seasonal run-off water from dams [9]. Sustainable groundwater abstraction should not exceed 3,650 MCM/yr. [9]. This amount covers renewable groundwater in Libya is 650 MCM/yr.; 25 MCM/yr. Hydrochemical studies of groundwater provide a better understanding of possible changes in quality [17]. The

chemical parameters of groundwater play a significant role in assessing water quality, which is suitable for drinking, agriculture and industrial purposes [15]; [32] ; [4] [29] Irrigation with poor quality water may bring undesirable elements to soil in excessive quantities affecting its fertility. The quality of groundwater has definite command over the yield of crops through its effect on environment. The main objectives of this study are to analyze the characteristics and assess the quality of the groundwater from aquifers using geochemical analysis and classifications to evaluate its suitability for drinking and irrigation purposes. The empirical classification has been adopted to indicate the nature and quality of the groundwater and determine the groundwater quality of Azintan's aquifers and delineate groundwater wells.

II. GEOGRAPHIC AND HYDROGEOLOGICAL SETTING

Groundwater in the study area is important resource for drinking water, agricultural, domestic and industrial purposes. The hydrogeochemistry and quality of groundwater in the study area are poorly understood and have not been investigated at depth. The study area lies between 31°51′54″-32°55′50″N 10°47′36″-12°14′54″E and covers an area of approximately 50 km². Azintan is one of the biggest cities in north western Libya in Jabal Nafusah, situated roughly 160 kilometers southwest of Tripoli. It is a rocky plateau, 600 to 700 m in its highest part, with a steep north face overlooking Jifarah Plain (Fig.1a) and gentle south slope ending along the northern edge of Al Hamadah Al Hamra. It has alluvial terraces, gently rolling hills and dry wadies (Fig. 1a). The average annual rainfall ranges from 100 to 250 mm per year, rainfall covers only the southern and eastern slopes of Jabal Nafusah [22]. The age of the outcropped rocks along Jabal Nafusah escarpment range from Jurassic to recent [12] (Fig.1b). The study area consists the Lower to Upper Cretaceous succession, has been divided into three major lithostratigraphic units (Nalut Formation; massive and crystalline dolomitic limestone and dolomite, Sidi As Sid Formation; has been divided into two Members: Ain Tobi and Yefren Marl, it consists dolomite and marl and Kikla Formation; includes sandstone).However, the study area is underlain by the alluvial deposit, which consists of sand and gravel. The thicknesses of the alluvial deposits range from 15 m to more than 50 m and are underlain by Mesozoic sandstone and limestone as bedrock (Fig 2).The major part of the study area, located in the Jifarah plain, which rises above sea level along the coast to 200 m at the foot of the Jabal Nafusah escarpment. The Jifarah plain is a triangular area of about

20 000 km², bounded on the north by the Mediterranean coast, on the south by Jabal Nafusah and on the west by the Tunisian border (Fig.1b). It is the most important part of the country for economic production and is one of the most intense areas for agricultural production in Libya. The Mesozoic sandstone rocks belong to the Kikla Formation, that are considered as one of the most potential groundwater reservoirs in Azintan.
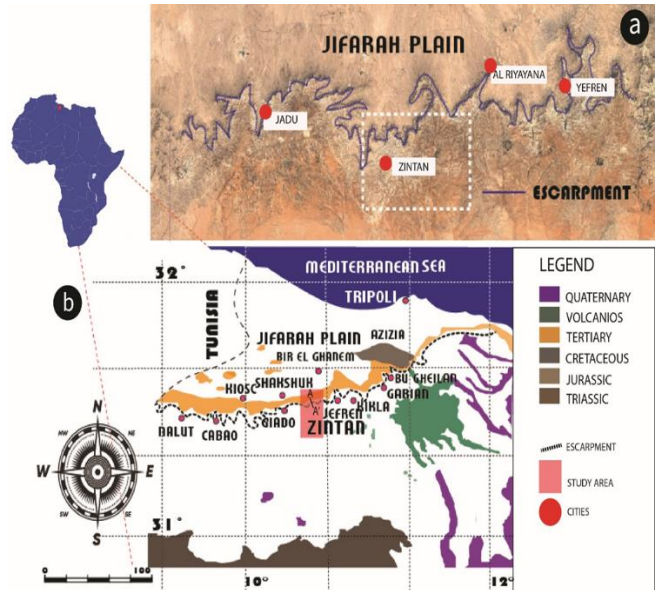

Fig.1 a. General location of Azintan area, and b. The geological map of study area (modified after [12]

The exploitable thickness of the undifferentiated formations is estimated to be around 50-100 m. The stratigraphic superposition in the area is illustrated by the north-south cross-sectional diagram (Fig.2). The Mesozoic sandstone Formation is widely distributed through this area and the undifferentiated Mesozoic sandstone strata overlain by the limestone rocks in the south direction (Fig.2). The rainfall varies between an average of approximately 100 to 200 mm/year in north of the Jifarah plain. There are few resources in the studied area. precipitation (Fig.3). The study area has an average of water levels within 100-200 m below surface.
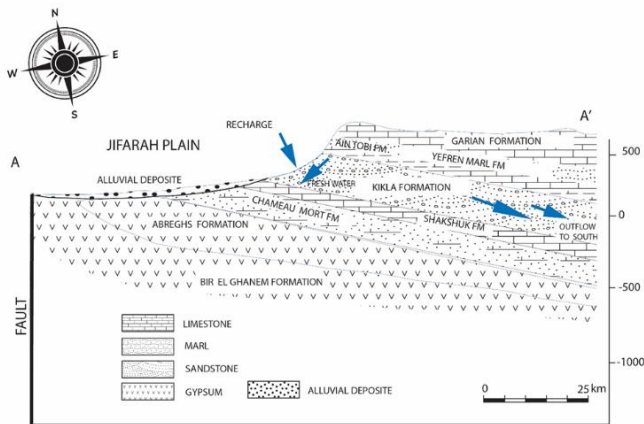
Fig. 2 Hydro cross section of A-A′. After [12]

The climatic factors of the study area are characterized by highly temperatures and high evaporation in the summer. The lowest and highest temperatures are usually observed in January and July, respectively (Fig.4). According to the data obtained from Azintan (weather station 2018), the average temperature is 17°C in the area. A part of the precipitation falling on the hills surrounding the Jifarah plain reaches the area surface runoff through many wadies, the length of which does not usually exceed a few kilometers. The loose sediments have been deposited in the area forming good water-bearing source. The major aquifers occur in north of Azintan city. The groundwater flow of the Azintan's aquifers covers extends south to north (S-N) direction (Fig.5).

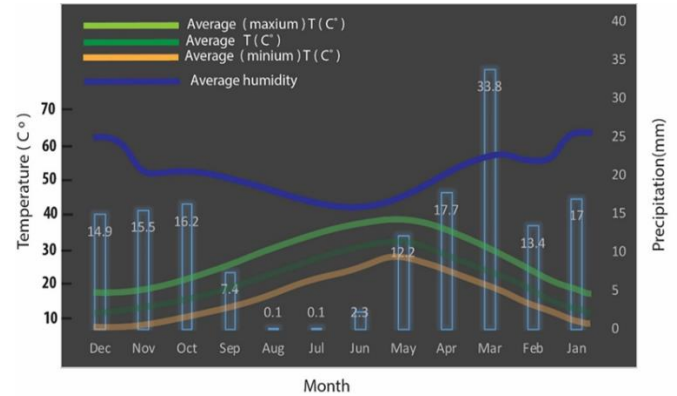Fig.3 Rainfall distribution and water level of the study area. [22].

Fig. 4 Monthly average temperatures and rainfall in the study area (Azintan weather station 2020).
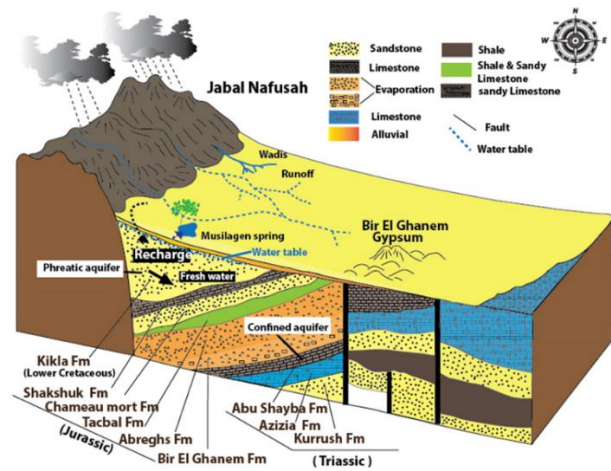

Fig.5 Conceptual model of the groundwater system at Azintan. Modified after [18]

The hydrogeological investigation indicates that there are three major aquifers throughout the area; the Kikla, Shakshuk and Chameau Mort. The stratigraphic section refers that Kikla Formation is lying at the top of the aquiferous Cretaceous Formation. Kikla Formation is one of the most potential groundwater reservoirs in the eastern part of Jabal Nafusah [18] and is tapped for the domestic water supply of Azintan. The Kikla Formation consists of Mesozoic sandstone (Fig.2) and is overlain by the rocks of the Sidi as Sid Formation (Ain Tobi Limestone and Yefren Marls members) and Garian Limestone. The depth of the water table varies between 50 to 100 m. The recharge of the Kikla aquifer is through infiltration of rainfall and wadi runoff. The transmissivity y (T) of the aquifer is $2\text{-}6\times10^2$ m²/s. The other major aquifer is Shakshuka Formation,
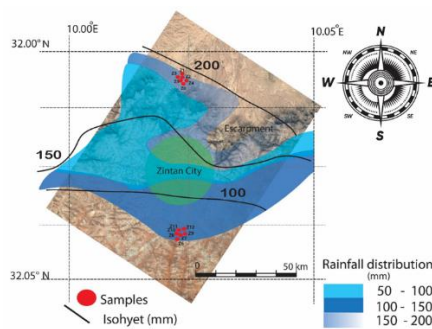
which is overlined by Kikla Formation, 80-110 m thick, which consists of variegated clay, limestone, dolomite and sand. This Formation shows good permeability, The transmissivity $T=2x10^{-3}$ m²/s, TDS: 2000 mg/L. Also, Chameau Mort Formation, 110-160 m thick, contains the main aquifer of the Jurassic group and consists of stondstone, and dolomite, which is alternated with clay. Its transmissivity values vary from 2x10-3 to $5x10^{-3}$ m²/s [18]. However, the Tacbal Formation shows a wide variety of permeability, the water quality is poor as total dissolved solids TDS> 2500 mg/L and becomes worse towards the bottom because of the increasing gypsum layers. Some 10 000 km² of the Jifarah overlies a system of freshwater aquifers. It can be assumed that the average rainfall is 200 mm/year. The overall volume falling on that area is about 200 x 106 m³. It is generally admitted that 10% of the rainfall percolates to the water table and recharges the unconfined aquifer [18]. Hence, the recharge of the freshwater aquifer system is some 200 x 106 m³ and the rest are evaportranspirated throughout the year.

III. MATERIALS AND METHODS

3.1. Sampling and analytical procedures

A total of 12 groundwater samples were collected from north and south of Azintan city.The north aquifer consists Lower Cretaceous sandstones (Kikla Formation), however, the south aquifer consists of hundreds of meters of Upper Cretaceous limestone. The samples were chosen carefully in order to evaluate the quality of groundwater in the study area. Major of the samples are located in the northern part of the study region, and the other samples were collected from the southern part. The samples were collected after removing the stagnant water.All groundwater samples were collected from hand-pumped wells. All groundwater samples were stored at approximately 5°C. The groundwater samples were analyzed at the water and gas analysis laboratory of Libyan National Oil Corporation in Az Zawiya and at the Engineering faculty lab in Sabratha. The research methods of collecting groundwater samples as well as the analysis of the water sample, followed standard procedure. The Ca^{2+}, Mg^{2+}, K^+ and Na^+ were analyzed using flame atomic absorption spectroscopy FAAS. HCO_3^- and CO_3^- were determined using acid titration method. Cl^- concentration was measured by $AgNO_3$ titration method, while SO_4^{2-} measured by Slaver 4 method HACH.

IV. RESULTS AND DISCUSSION

4.1 Hydrochemical modelling and charac-teristics.

Interaction between water and surrounding rocks and soil is considered to be the main process controlling the observed chemical characteristics. The deviation of water from equilibrium with respect to dissolved minerals is quantitatively described as follows.

4.1.2. Saturation index (SI)

The calculation results of SI are listed in Table 1. calculated according to the formula; saturation Index $=lg10(IAK/K)$, Where IAK is Ion Activity Product of dissociated chemical species in solution. K is equilibrium constant product of chemical involved [1]. The hydrogeochemical equilibrium phases, [25] were used to calculate the SI of water with respect to the main mineral phases by phreeqc software. The SI values of calcite, dolomite and gypsum for most groundwater samples are greater than zero, indicating supersaturation of these sulfate and carbonate minerals. Equilibrium is taken to be between SI = -0.1 to 0.1 [2]. Using saturation index approach, it is possible to predict the reactive mineralogy of the subsurface.

(Table 1) Calculated saturation indices of calcite, gypsum and dolomite

Calcite	Gypsum	Dolomite
SI	SI	SI
0.86	1.38	0.83
0.56	1.30	0.60
0.41	1.20	0.47
0.514	1.00	0.38
0.59	1.14	0.46
0.84	1.45	0.72
0.63	1.33	0.54
0.85	1.45	0.76
0.31	1.11	0.49
0.84	1.33	0.83
0.70	1.20	0.65
0.81	1.15	0.83

In the recharge zones, groundwater is gypsum-saturated, dolomite and calcite in the up gradient areas of a regional flow, due the interactions with sufficient mineral and ionic sources. This interaction will be taken place, and reach equilibrium with these minerals. Due to progressive mineral

dissolution the TDS in groundwater will also increase along the groundwater flow path. Therefore, the plot of TDS versus SI (Fig. 6) suggests the evolution along the flow path. The SI values of calcite and dolomite range from 0.31 to 0.86 and from 0.38 to 0.83, respectively. The correlations between them and the TDS are not significant (Fig.6), which indicate that calcite and dolomite (carbonate minerals) do not continue to dissolve along the flow path. In contrast, the SI value of gypsum is more than one, and all minerals exhibit positive correlations with TDS (Fig. 6), which suggests that the SI values for aragonite, calcite, dolomite and most magnesite were greater than zero. Thus, water is supersaturated with precipitation of calcite, dolomite or gypsum. The Ca^{2+} will increase in groundwater due to dissolution of gypsum, which will in turn increase the SI values of calcite and dolomite. The decrease in the SI values of calcite and dolomite may support this inference (Fig. 6).

4.1.3. Sodium Adsorption Ratio (SAR)

The soluble sodium percentage (Na%) and the Sodium Adsorption Ratio (SAR) are used for determining the suitability of groundwater for agricultural uses. However, medical research restricts sodium content in drinking water to 120 mg/l [5]. Both are considered a useful indicator in determining the suitability of groundwater for agricultural uses. In this study, the values of SAR and EC were plotted on salinity diagram (Fig. 7) combining the two hazards, sodium and salinity, the results show that most groundwater samples belong to the category C3-S1 (low sodium and high salinity). Theoretically, can be used with caution for agricultural purposes. Z-1, Z-10, Z-11 and Z-12 belong to C4-S2, indicate that although these samples represent low alkalinity hazard, and they are not suitable for irrigation under ordinary conditions because they represent a very high-salinity hazard. In this study area, all samples are not exceeding the limit, which may affect consumers. Depending on Libyan standard [21], it was found out that some groundwater samples were suitable for drinking; as soluble ions not exceed the maximum permissible limit. Exceed salinity reduces the osmotic activity of plants and interferes with the absorption of water and nutrients from soil (Saleh and Shehata, 1999). Salinity, Sodium absorption ratio (SAR) and sodium percentage (Na %) are important parameters for determining the suitability of groundwater for irrigation uses [30]. Sodium concentration is a n important factor in classifying irrigation water, because sodium reacts with soil to reduce its permeability. All ionic concentrations are expressed in milli-equivalents per liter (meq/L).Generally, when Na% value is less than 60%, it is acceptable for

irrigation. Most of samples are plotted in zones of excellent to good, good to permissible and unsuitable zone [37]. The Sodium percentage is computed with respect to the relative proportions of cations present in water, where the concentration of ions is expressed in meq/L using formula after [23].
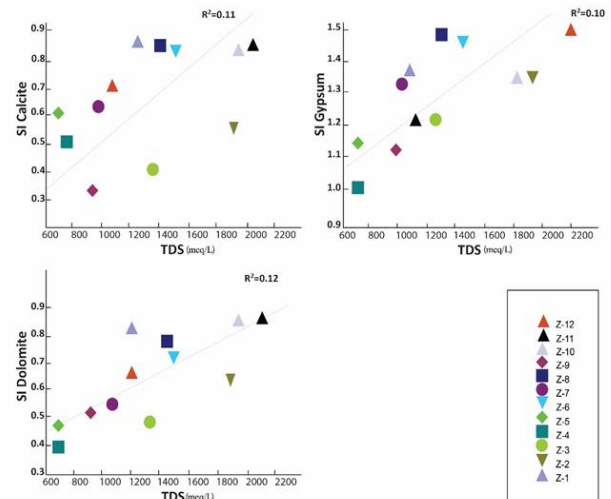

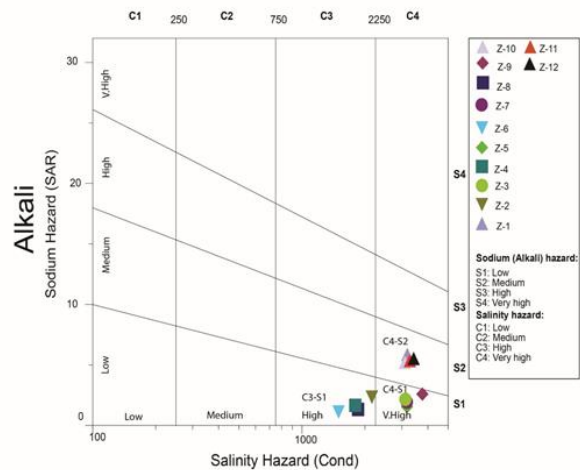Fig. 6: Plot of SI of Calcite, Gypsum and Dolomite minerals versus TDS (meq/L).

Fig. 7 Classification of groundwater, based on Salinity and Sodium Adsorption (SAR), [33]. Samples belong to the category C3-S1 (low sodium and high salinity), C4-S1 (

low sodium and very high salinity) and C4-S2 (very high salinity with medium sodium).

Samples Z-1, Z-2, Z-10 and Z-12 belong to unsuitable category (Fig. 8), indicating that they are not suitable for irrigation. The classification of groundwater samples with respect to sodium percentage are shown in (Table 2). Only four samples have values ranging between 23 to 29 %, which indicate values larger than or equal to 20%, whereas eight samples have values ranging between 30 and 55%. Most values generally less than 60%, indicating that they are all safe to be used for irrigation purposes. Exceed Na+ combining with carbonate lead to formation of alkali soil, whereas with chloride, saline soils are formed [27]. According to classification of hardness [29]and (Table 2), all samples fall under very hard water category. The chemical analysis revealed that the total hardness of $CaCO_3$ varied from 500 to 1140 mg/l for both samples, indicating very hard water (Fig.9). The hard water noticed in most of the samples, could be attributed to calcareous soil and limestone units found in the study area. The Ca2+ salt in most of the groundwater samples suggests a calcareous aquifer. The plot of total hardness (TH) versus total dissolved solids (TDS) (Fig.9a) shows that the groundwater samples lie in brackish zones to the fresh, indicating different quality levels. However, the other samples are too hard (Fig.9b). To detect mechanisms that control the hydrochemical components in surface water and groundwater, Gibbs diagram is used (Gibbs 1970). The total dissolved solids are plotted against ratios of cations $[Na^+/ (Na^+ + Ca^{2+})]$ or anions $[Cl^-/ (Cl^- + HCO3^-)]$. The diagram is divided into three zones representing different controlling mechanisms which are evaporation, rock, and precipitation (rainfall) dominance. Gibbs diagram (Fig.9) shows that all the water samples fall entirely in the zone between the evaporation and rock dominance zone which is compatible with storage conditions. The TDS increase in irrigation water affects soil efficiency and growth and yield of plants. For long term irrigation under average conditions, the total dissolved solids should not exceed 2000mg/l. High increase in water salinity increases salts amount in soil and leads to salinization problem. Classification of water according to hardness [29] is given in Table 3.
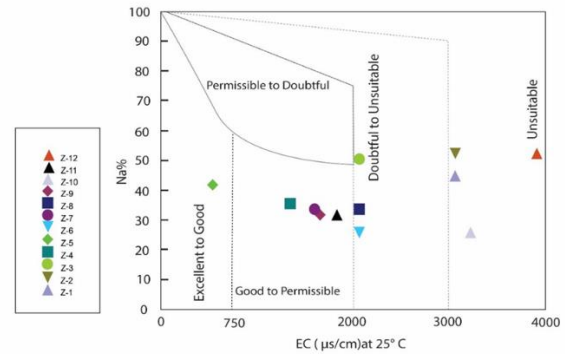

Fig. 8 Plot of Na% versus EC, (Wilcox, 1948)

Table 2. Classification of groundwater, based on Sodium percentage after [37]

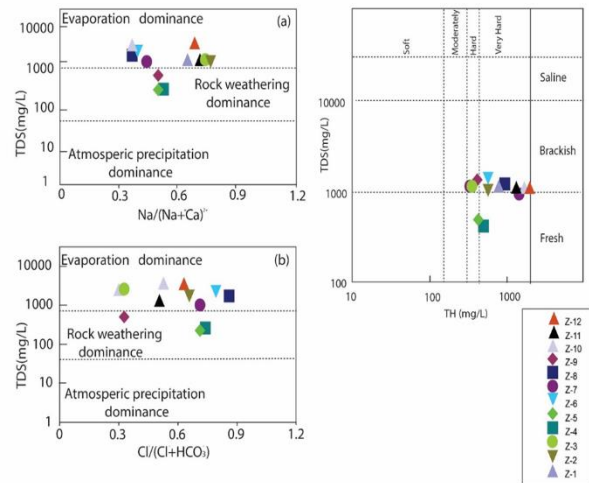| Sodium (%)	Water	Samples
<20	Excellent to good	Z-9
20-40	Good to permissible	Z-4, Z-7, Z-9, Z-11
40-60	Permissible	
60-80	Doubtful	Z-6, Z-8, Z-3
>80	Unsuitable	Z-1,Z-2,Z-10,Z-12

Fig.9: a) Plot of TDS versus TH expressed in mg/L as $CaCO_3$. b) Gibbs diagram shows TDS versus $Cl^-/ (Cl^- + HCO3^-)$ and $Na^+/ (Na^+ + Ca^{2+})$.

Table 3. Classification of water based on hardness after [29]

Hardness as CaCO₃	Water class	
0-75	Soft	
75-150	Moderate Hard	
150 - 300	Hard	Z-3,Z-7 and Z-9
>300	Very hard	The rest of the samples

V.   RESULTS

The analytical results of the physiochemical and the statistical analysis indices are shown in Table 4&5. The TDS in the groundwater ranges from 676 to 2240 mg/L, indicating fresh to brackish mineralized water (TDS < 3000 mg/L; Aral and Warren 2001). The EC of the groundwater is higher than that of the surface water, suggesting mineral dissolution in the groundwater, EC ranges from (965 to 3730 μs/cm).

All samples fall under low saline water (Banks and Siewers, 2001). Among the mean ion concentrations, the main anions are SO_4^{2-} and Cl^- with averages of 345.80 and 418.917 mg/L, respectively. The HCO_3^- ranges from 191 to 502 mg/L. The main cations are Na^+ and Ca^{2+} with averages of 171.198 and 124.156 mg/L, respectively. The pH of the groundwater is within the range of 7.4 to 8.3, indicating an alkalescent tendency. All samples are compared to Libyan and WHO guidelines see Table (4). The groundwater samples have low value of total dissolved solids as compared with other major groundwater reservoirs samples throughout the country. The relative high-water levels within the aquifers and negative effects of sediments are responsible for the low value of TDS. Total Hardness ranges from 384.35 to 1140 mg/L and is therefore it is categorized as very hard water according to [29]. No ammonia nitrogen and nitrate nitrogen pollution were detected. Tri-linear diagrams are perhaps the most commonly used technique for finding hydrochemical patterns in major ion data.In the present study, a Piper diagram [26] was used to determine the major hydrochemical facies. It shows that SO_4^{2-} and Ca^{2+} are the main hydrochemical facies in groundwater. Accordingly, two water types were recognized in this region. These are Cl-SO4-Na-Ca and Cl-SO4-Na. The first type (Cl -SO4-Na) belongs to well of Z-1, Z-2, Z-3, Z-4, Z-5, Z-10 and dominate source of this facies comes from dissolution of limestone and marl in the study area. The second type belongs to the wells Z-6, Z-7, Z-8, Z-9. The dominant

source for this facies comes from dissolution of limestone, dolomite and calcarenite.

5.1 Correlation of major chemical indices

Multiple correlations are useful to interpret the major hydrogeochemical evolution processes within an aquifer and can also be used to deduce the sources of ions and the origin of the groundwater and to measure and establish the relationships between average variables. It also helps to distinguish the relevant hydro geochemistry facias. The multiple diagonally symmetrical linear correlation matrices of Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, Cl^-, CO_3^-, pH, EC, TH and TDS of the study area samples are given in (Table. 6). The relation between the variable Na+ vs K^+ show positive correlation. The Na^+ and K^+ are mainly obtained from the weathering of calc-alkaline group of rocks and carbonate sources are mainly obtained from the per alkaline group of rocks.

The relationship of variables in the study area also shows existing same positive correlation, except HCO_3^- , K^+ and vs TH, which shows a very low degree of insignificant negative correlation. The correlation studies between TDS vs K^+, Na^+, Ca^{2+} and Mg^{2+} show positive correlations which indicate that the combined operation of chemical weathering, groundwater movement and controlled the chemistry of groundwater in the study area.

The cluster analyses of geochemical parameters of the study area is performed for ionic concentration on the elements of hydrogeochemistry of groundwater and for classify cases of groups that are relatively heterogeneous between each other, on the basis of a defined set of variables. The cluster analyses have been performed using SPSS software and Ward's method. The average parried groups of ionic clusters of geochemical parameters are (Mg^{2+}, Ca^{2+} ,SO_4^{2-}, CO_3^-), (Cl^-, HCO_3^-, CO_3^-, TDS, K^+), (pH, Na+, EC) and (TH) Fig 11. First cluster includes the sample locations of Z-4, Z-5, Z-7 and Z-9. The second cluster consists of the sample locations of Z-6, Z-8, Z-11 and Z-3. The third cluster involves the sample locations such as Z-1, Z-2 and Z-10. The fourth cluster consists of the sample locations of Z-12.
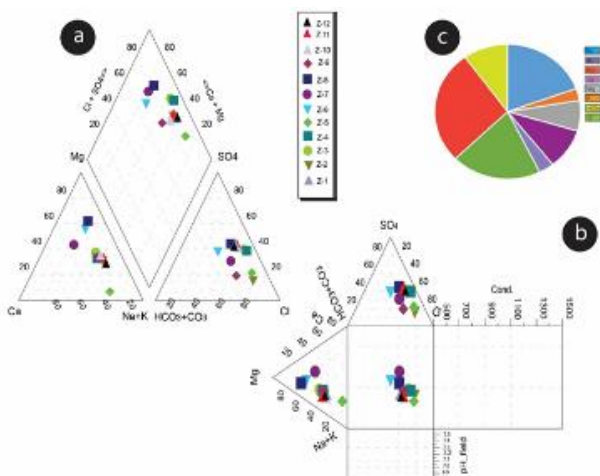
Fig. 11. Trilinear Diagram of the major ions in the groundwater of Azintan area.

Sample	pH	TC°	EC	TDS	TH	Na+	K+	Mg2+	Ca2+	Cl-	SO42-	HCO3-	CO3-
Z-1	7.5	22	3190	1910	920	409	60.8	153.52	205	420	426	210	0
Z-2	7.6	22	3108	1860	700	362	58	126.7	103	368	521	191	0
Z-3	8.3	22	2160	1296	500	221	52.1	78.16	71.2	250	430	502	4
Z-4	7.74	22	995	686	384.4	118.87	56.96	37.33	92.34	262.7	153	79.09	0
Z-5	7.67	21	965	676	461.2	132	34	44.79	110.8	213	264	89.64	0
Z-6	7.22	21	2087	1461	860.9	121	30	89.59	196.98	568	613	137.1	0
Z-7	7.28	20	1493	1060	568.8	110	28	63.46	123.11	298.2	525	126.5	0
Z-8	7.2	22	2006	1360	953.2	105	26	108.25	203.14	568	575	84.36	0
Z-9	7.9	22	1498	899	550	75.5	20.8	99.64	55.8	220	360	366	4
Z-10	7.8	22	3180	1910	1140	131	37	155.34	200	348	320	321	0
Z-11-	7.8	22	1857	1115	920	122	27.7	183.8	65.1	288	450	219	4
Z-12	8.1	22	3730	2240	420	147	29	63.47	63.4	420	426	210	0
average	7.68	21.67	2189.08	1372.75	698.2	171.2	38.36	100.34	124.16	352	421.92	211.3	1.09
Liby.stand.	6.5	-	750	> 1000	300	200	40	150	200	250	400	-	-
WHO2017	-	1500	500-1500	100-500	200-600	10=12	50-100	75-200	250-500	200-250	200-500	-	-

Table 4 Results of the physiochemical analyses (mg/L)
Table 5. The statistical analysis results.

| Samples	Z-1	Z-2	Z-3	Z-4	Z-5	Z-6	Z-7	Z-8	Z-9	Z-10	Z-11	Z-12
Na%	49.38	57.42	52.31	38.91	41.05	27.65	33.89	23.73	29.99	25.03	30.61	48.54
MH(Magnesium Hazard %)	42.82	51.05	52.33	28.79	28.79	31.26	34.01	34.76	64.1	43.72	73.84	50.03
SAR%	10.8	12.48	9.04	5.22	5.29	3.57	4.03	2.98	3.03	3.47	3.87	6.53
Na/(Na+Ca) meq/L	0.67	0.78	0.76	0.56	0.54	0.38	0.47	0.34	0.58	0.4	0.65	0.7
Cl/(Cl+HCO3) meq/L	0.67	0.66	0.33	0.77	0.7	0.81	0.7	0.87	0.38	0.52	0.57	0.56
HCO3 meq/L	3.44	3.13	8.23	1.3	1.47	2.25	2.07	1.38	6	5.26	3.59	4.2
Ca meq/L	10.25	5.15	3.56	4.62	5.54	9.85	6.16	10.16	2.79	10	3.26	3.17
Mg meq/L	12.64	8.84	6.43	3.07	3.69	7.37	5.22	8.91	8.2	12.79	15.13	5.22
Ca+Mg meq/L	22.89	13.99	9.99	7.69	9.23	17.22	11.38	19.07	10.99	22.79	18.38	8.39
Cl meq/L	11.86	10.4	7.06	7.42	6.02	16.05	8.42	16.05	6.21	9.83	8.14	9.15
Na meq/L	17.78	15.74	9.61	5.17	5.74	5.26	4.78	4.57	3.28	5.7	5.3	6.39
SO4 meq/L	2.66	3.26	2.69	0.96	1.65	3.83	3.28	3.59	2.25	2	2.81	2.44
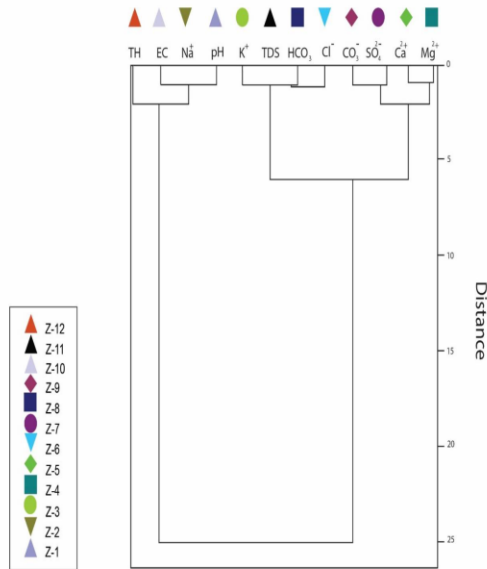
Fig.11 Dendrogram of groundwater aquifers in Zintan.

Table 6. The multiple correlation matrix of water quality parameters.

Continue.

3-	EC	TDS	TH	
-0.1	1			
-0.2	0.99	1		
-0.1	0.37	0.4	1	

The ratio of Na and Cl^- in meq/L should be equal to 1, if Cl^- and Na^+ are derived solely from the dissolution of halite. Most samples are plotted below the 1:1 line (Fig. 12a), which indicate that the Na+ is lower than Cl- content due to the cation exchange makes Na+ in groundwater (Fig. 12a) Furthermore, $(Ca^{2+} + Mg^{2+})$ versus HCO3- (Fig.12b) plot shows that the samples plotted below 1:1 and 1:2. The content is slightly in excess of HCO3- due to role of silicate weathering as the primary mechanism for the occurrence of dissolved salts in the groundwater and indicating that the dissolution of dolomite is likely to occur in the area. In summary, the dissolution of carbonate minerals (calcite and dolomite) may make important contributions to the Ca^{2+}, Mg^{2+} and HCO3- in groundwater. Similarly, if the dissolution of gypsum is the only explanation to the origin of Ca^{2+} and $SO4^{2-}$, the ratio of Ca^{2+} and $SO4^{2-}$ in meq/L should be 1:1 (Fig. 12c). Gypsum is oversaturated in the groundwater, and their dissolution can be a significant contribution to the increasing content of Ca2+ in the groundwater.

5.2 luster Analysis

However, the calcite is saturated, therefore, calcite precipitation is most likely the most appropriate explanation for the Ca^{2+} deficiency versus $SO4^{2-}$ (Fig. 12c). The slope for HCO3- against Ca2+ should range from 1:1 to 1:2. (Fig.12d).
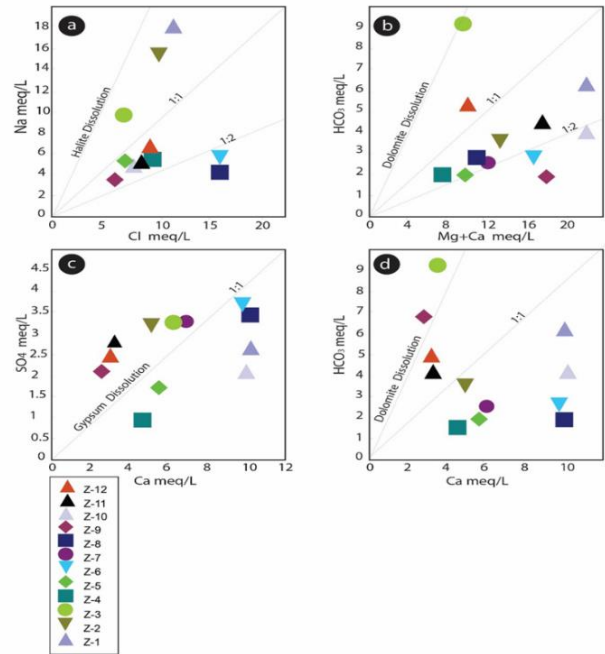

Fig.12. Relationships among major ions in groundwater samples.

1	pH	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	$SO4^{2-}$	HCO_3
pH	1							,
Na+	0.01	1						
K^+	0.16	0.79	1					
Mg^{2+}	-0.06	0.34	0.03	1				
Ca^{2+}	-0.69	0.19	0.09	0.29	1			
Cl^-	-0.58	0.11	-0.11	0.20	0.694	1		
$SO4^{2-}$	-0.48	0.14	-0.27	0.29	0.329	0.68	1	
HCO_3^-	0.728	0.13	0.087	0.26	-0.31	-0.3	-0.04	1

VI.   DISCUSSION

The important hydrogeochemical parameters in assessing water quality are TDS, EC and SAR, which reflect the classifications of irrigation and drinking water quality. The values of SAR (Table 5) and EC (Fig.7) show that most groundwater samples belong to the category C3-S1, which is suitable for agricultural purposes. The poor quality of the groundwater is controlled by levels of TDS, TH, Cl- and SO4²⁻, which result from the dissolution of various mineral phases in the aquifer. Sulfate content ranges from 153 to 613 mg/l with average of 421.92 mg/L. The increment of sulfate toward southern part >450 mg/Lis mostly due to dissolution of gypsum minerals. and also, due to extension of gypsiferous limestone. The sulfate ions reached the groundwater system. The percolating water usually dissolves completely all highly salts such as NaCl, but partially dissolve sparingly soluble salt such as gypsum [11]. However, toxicity is rarely a problem, except at very high concentrations, where high sulfate may interfere with uptake of other nutrients. Although chloride is essential to plants amounts, it can cause toxicity to sensitive crops such as fruit and vegetable crops at high concentrations Table 7 [6].

However, in the northern area, the groundwater has EC values between 670 to 2000 as/cm (except sample Z-1 and Z-2), indicating excellent and good to permissible utility for irrigation.

Table 7. Chloride classification of irrigation water.

Chloride (mg/l)	Effect on crops	Samples
< 70	Generally safe for all plants	
70-140	Sensitive plants show injury	
140 - 350	Moderately tolerant plants	except Z-1,Z-2 Z-12
>350	Can cause severe problems	Z-1, Z-2,Z-12

Another indicator that is used to specify the magnesium hazard (MH) as proposed by [31] for irrigation water (Table 8). From the calculated values, the magnesium hazard values range between 28.7 and 73.84 (Table 9). A value of MH > 50 % indicates harmful groundwater and unsuitable for irrigation, while a value MH< 50% indicates suitable groundwater.

Table 8. Sodium hazard classes based on sodium adsorption ratio after [37].

Sodium hazard class	SAR	Water class	Study samples
S1	10	Excellent	Z-7, Z-8, Z-9, Z-10, Z-11, Z-12
S2	10-18	Good	Z-2,Z-4,Z-5
S3	18-26	Doubtful	Z-1,Z-2,Z-3
S4 and S5	> 26	Unsuitable	

Table 9. Water quality based on magnesium hazard after [37].

Magnesium hazard	Water class	Remark
<50%	Suitable	Z-1, Z-4, Z-5, Z-6, Z-7, Z-8, Z-10
>50%	Unsuitable	Z-2, Z-3, Z-9, Z-11, Z-12

VII.   CONCLUSIONS

The study area is a terrain which consists of sandstone rocks and crystalline limestone and dolomite and evaporite rocks. Gibbs mechanism reveals evaporation and rock dominance character controlling water chemistry. Geochemical evaluation through Piper analysis shows the predominance by higher concentrations of Cl^--SO_4^{2-}-HCO_3^-, Cl^-- SO_4^{2-}-Na^+-Ca^{2+} and Cl^-- SO_4^{2-}-Na^+ rich facies. Groundwater samples generally show within the permissible limit of Libyan standards guidelines and WHO drinking water standard except pH, EC, TH, SO_4^{2-} and Cl^- .The majority of samples are suitable for irrigation purposes. Groundwater quality may be enhanced by river basin recharge.

Acknowledgements

VIII.   REFERENCES

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