



Describe and Statistical Evaluation of Hydrochemical Data of Karst Phenomena in Jordan: Al-Dhaher Cave Karst Spring

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Abstract: Karstification in Al-Kura District, northwestern of Jordan, is distribution in the Tertiary rocks at chalky and marley-limestone unit and it forms a local shallow unconfined aquifer. This research is constructed to describe and study the hydrogeochemical of karst features and their effects on the hydrochemistry of the Al-Dhaher Cave. Studied samples were collected from the water of wells and springs in the study area. All types of water have a composition in milligram units for cations ($\text{Ca}^{2+} > \text{Mg}^{2+} > (\text{Na}^+ + \text{K}^+)$), and anions ($\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$). Calcium and bicarbonate accounts approximately 80% of the total ions. The concentrations of Ca^{2+} and Mg^{2+} are strongly correlated with HCO_3^- . The $r\text{Ca}^{2+}/r\text{Mg}^{2+}$ ratio for Al-Dhaher Spring is about 1.54, which suggests that water moves in chalky and marly limestone. Our data revealed that the main ions Ca^{2+} , Mg^{2+} , and HCO_3^- have very strong correlation to spring discharge. The water is undersaturated with respect to calcite and dolomite, and the correlation of SIC and SID to discharge is very strong ($r=0.97$ and 0.96). Depending on comparing the coefficients variations, the type of Al-Dhaher Spring could be classified as conduit spring. The results of water analyses studies show that the aquifer system is prone to karstification and they show the impact of karstification on the chemical composition of spring waters.

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Short Title: Hydrochemical Data of Jordan Karst

Introduction

Rain and snow fall on many parts in the world in winter absorbing carbon dioxide out of air and soil, turning it into weak carbonic acid, which contribute to purity of winter water. As watercourses sink through cracks very fast, there are no surface flows in karst, which is one of its basic features, instead there are subterranean water flows dissolving rocks and expanding cracks, and in that way forming numerous caves, holes, and pits (Dreybrodt and Gabrovšek, 2003; Lauritzen, 2005).

Karstification involves dissolution of the bedrock by means of water and acids that are transported into the rock mass (Bosák, 2003; Filipponi and Jeannin, 2008). Dissolved materials are transported out of the karst, and the water-flow through the karst is driven by gravity (Kiraly, 2003; Lauritzen, 2005; Aloui and Chaabani, 2007; Papadopoulou et al., 2007; Rashed, 2012).

In the last years, many geologists groups has carried out multidisciplinary studies in geology, hydrochemistry, and microclimate at different caves located in Spain, such as: Altamira (Cañaveras et al., 1999; Papadopoulou et al., 2007), Tito Bustillo (Cañaveras et al., 2001), Candamo (Groth et al., 2001). Other different caves located in Italy such as Grotta dei Cervi (Sanchez-Moral et al., 2003) and Saint Callixtus Catacombs (Groth et al., 2001), and other karst caves such as Iskrets karst spring located in Bulgaria (Eftimi and Benderev, 2007).

Howard (1964) reported that the first stage of karst initiation could be enhanced by local acid production. Others suggested mechanisms of water penetration and initiation of karst formation, which is started in convergence of flow, addition of fresh solutions, and enhanced solutional ability (Bogli, 1964; Howard, 1966; Runnells, 1969; Dreybrodt, 1981; Bosák, 2003; Dar et al., 2011).

Jagnow (1977), Jennings (1985), Hill (1987), Polyak et al. (1998), and Dar et al. (2011) had discussed many details about geological history of Carlsbad Cavern caves. These caves have been formed in a thick, dolomite-rich carbonate rock sequence and contain abundant chemical sediments known as speleothems, which contain a variety of Mg-bearing minerals like trioctahedral smectite in Mg-rich carbonate speleothems (Polyak and Güven, 2000). Furthermore, authigenesis of trioctahedral smectite in caves has been reported only in Bulgaria, Romania, and Turkmenistan (Hill and Forti, 1997). Abu-Jaber et al., (2006) were the first to present a detailed geological and climatological data about Al-Dhafer Cave sediments in Jordan.

Emphasis in this work is placed on studying the cave system in Al-Kura Reserve, during these main objectives:

(a) To investigate, characterize the hydrochemistry of springs water and wells, and to establish some of the processes taking place within the aquifer, including the possible influence of the intensive abstractions on mineralization of the groundwater. (b) Water quality variation of Al-Kura karst springs. (c) To describe the physical aspects of the karst, (d) To study the effect of solutions passage within the joints and fractures at the carbonate rocks and relations with karstification phenomenon, and finally (e) To study the geological setting and providing net water in the study area on the quality of the drinking water.

Study Area:

The studied area was the Berqish Reserve aquifer, which is a small karstic aquifer occupying a surface area of approximately 20 km² at the north flank of Ajloun Dome, North of Jordan (Fig. 1a).

Limestone and marly limestone formations are found in many parts of North Jordan, mostly with deep reaching karst features. Typical of the underground regimes of such massives are small hydraulic gradients, depending on the degree of karstification. This is why groundwater flow is often observed over many distances into neighboring catchment areas. The deep wells tap the Tertiary regional aquifers; while the springs and wells discharge, perched aquifers of Quaternary age (Late Pleistocene).

Physical Setting

Al-Dhafer Cave karst, which was discovered in 1995, is located in Al-Kura District, about 25 km southwestern of Irbid (Fig. 1a). Al-Dhafer Cave is a structural cave mainly formed along two fault systems, one with a N70°W trend and a second with a N45°E trend (Abu-Jaber et al., 2006). Its area is about

4000 to 5000 m² and catchment area is about 20 km² and has mountain relief. The altitude of the studied area is from 600 m up to 950 m. The highest part looks like a plateau tableland with longitudinal hills and smaller plateaus on them surrounding with lowest elevation.

Climate of the region is classified as a typical Mediterranean climate, with warm dry summers and cool rainy winters. According to the data from a Meteorological Department, Open Files 2007 to 2010, the mean annual precipitation is about 600 mm/y. The most intensive precipitation within the period of December, January, and February reaches up to 75% from yearly total precipitation. The snow cover at the highest altitudes in the study area in winter seasons plays a significant role in ground water recharge, and it could be available approximately to the end of the spring season while the mean annual temperature is about 15°C.

The springs of AL-Dhafer, Ain Zubia, and Ain Zgaeg are located in the center of the Al-Dhafer Cave area, near Zubia village, and west of Kufraheel village. In addition, two valleys flow in the study area: (1) Wadi Al Rayan: located in the west of Judita village, and it has got always outflow under the Al-Dhafer Cave and Ain Zgaeg, (2) Sahel Al Nuhaier located in the north south of Kufraheel village, near the Al-Dhafer Cave area. These wadies and springs are the main basis of erosion in this region and its basin is developed completely on karst rocks (Fig. 1b).

Hydrogeologically, the catchment area of the studied area springs are divided into two zones. The first includes outcrop of karst sediments without any river runoff. The second one is located below the first zone at lower altitude of karst phenomenon, and it consists of non-to semi, karstified rocks and some small water pathway are flowing there.

The total length of Al-Dhafer Cave is about 130 m. The entrance is a vertical about 2 m deep shaft with a diameter of 1 m. The cave consists of the main cave passage, which is typically 1 to 2 meters wide and 2 to 4 meters high. There are a number of large halls and a few branches and passages.

Geology and Hydrogeology

Geologically, the region consists mainly of Upper Cretaceous limestone, known as massive limestone unit (Bender, 1974), or Wadi Sir Formation (Masri, 1963), or A7 Formation (Wolfart, 1959). Karst processes are found out into two carbonate complexes: Wadi Sir Formation (A5/A6 and A7), consisting of massive white microcrystalline limestone, dolomitic limestone. Ruseifa Formation (B1) consisting of a thick bed of marly limestone with a thin bed of marl and chalk. The extensive fractures

and karst development position and interaction between these two complexes are controlled by tectonic conditions in this part of the study area (Mikbel and Abed, 1984).

Hydrogeologically, aquifers in the most of the areas of North Jordan are divided into two major and three minor aquifers according to their water supply (El-Naser, 1991), separated from each other by a thin or extensive aquicludes. The Fuheis Formation (A3) marl aquiclude separates the Kurnub aquifer from the karstified dolomitic limestone aquifer of Al-Hummar Formation (A4), which is considered as a minor aquifer in the study area.

The focus of the study is Wadi Sir Formation which is considered as one of the most important aquifers in northern Jordan, and the two-carbonate complex is the most important, which is discharged by Ain Zubia and Ain Zgaeg springs. This is because of the extensive fracturing and karst development which it underwent, allowing for the formation of the porosity needed to become aquifer. The overlying limestone of Upper Cretaceous carbonate complex outcrops as some spots forming some small isolated and completely discharged karst massive. They facilitate the intensive infiltration of the precipitation. Wadi Al Rayan and Sahel Al Nuhair coming from the northeastern parts of Al-Kura district and sinking in the north and south areas of the complex have a significant role for groundwater recharge (Fig. 1b). The groundwater flow direction is from east to west – to cave spring, Ain Zubia, and Ain Zgaeg springs. The available information on the hydraulic properties of Wadi Sir Formation aquifer in the study area is very limited and is unable to give a satisfactory picture of the hydrologic situation.

The case in the study area is not different from the other karstic aquifers around the world. Wadi Sir Formation aquifer (A7) receives water directly from rainfall, and discharges it through springs; some of them can be considered as karstic springs like Al-Dhaher Cave Spring, Ain Zubia, and Ain Zgaeg. Springs in the study area display almost the same pattern of discharge fluctuation, indicating the same or similar recharge-discharge mechanisms of other springs in the region.

Al-Dhaher Cave, How It Was Formed?

The land of Al-Kura district mostly is a fully developed karst relief gradually formed as a consequence of various geological factors, including the bedrock material and tectonics, as well as climatic conditions. Al-Dhaher Cave karst is the most extensive and most developed karst area of the Al-Kura district (Bosák, 2003; Kempe et al., 2006).

The main classification type of cave in the study area is a solution cave formed in carbonate

rocks (Sadiq and Nasir, 2002) by the action of slowly moving surface and ground water that dissolves the rock to form tunnels, irregular passages, and even large caverns along fractures, joints, faults and bedding planes (Fig. 2).

After rain on the ground, the water starts infiltration in the vadose zones to the subsurface beds, seeps into cracks and pores in the soil cover, and passing through the faults, fractures, and joints dissolution spaces got larger and would be more split and more connected (Kiraly, 2003; Screaton et al., 2004; Aloui and Chaabani, 2007; Papadopoulou et al., 2007). Eventually some of the water reaches a zone of water table where all the cracks, pores, faults, fractures, and joints in the limestone rocks are already filled with water and become dissolved and saturated in the carbonate ions (Screaton et al., 2004). This causes the formation of stalactite and stalagmite deposits downward from the ceiling and upward over the floor of the cave, respectively. The resulting of calcium bicarbonate solution is carried off in the underground drainage system (Screaton et al., 2004; Papadopoulou et al., 2007).

Stalactite and stalagmite in Al-Dhaher Cave both grow as a concentric layers and as a cylinder shape and may reach lengths to several meters with more than one meter of base diameter (Fig. 3). Curtain shape is formed of a wavy or folded sheet hanging from the upper roof or wall of a cave to about 2 to 3 meters long and about 1 to 1.5 meters width. Curtain developed where the feed water trickles down an inclined wall (Fig. 4). Some shallow and small caves in the study area are distributed near and around the Al-Dhaher Cave and formed near the earth's surface - above the saturated zone- where the water moved downward through the cracks, pore spaces, joints, and fractures.

Methodology

The springs in the study area were examined continuously over three consecutive years, in order to identify the chemical water during different seasons of the year (summer and winter). A number of graphs were constructed in order to clarify the correlation between the concentration of different ions in the water, and linking it with the ability of discharge water springs during the different seasons to determine the most important factors affecting corrosion of carbonate rocks through time, and thus build the karst caves in the region. Particular attention was paid also to calcite and dolomite equilibrium of spring's water.

Samples were collected during 2007-2010 as presented in Tables 1 to 4. All study samples of springs were taken in the only available way at the spring's pipe mouth.

Fifty-five water samples were collected, 20 samples from 8 different wells distributed through the study area, and 35 samples were collected as followed: 5 samples from Al-Dhaher Cave Spring, 15 samples from Ain Zubia, and 15 samples from Ain Zgaeg. The last two springs flow near Al-Dhaher Cave. Ain Zubia connected with Al-Dhaher Cave Spring along hydrogeological aquifer, supplying it with water during all of the spent time.

Temperature, electrical conductivity, and pH were measured using standard electrodes. The major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) were analyzed using Atomic Absorption Spectroscopy (AAS, model Philips SP 9PYE Unicam Spectrophotometer), anions such as bicarbonate (HCO_3^-) and chloride (Cl^-) were analyzed using standard titration techniques, while sulfate (SO_4^{2-}), and nitrate (NO_3^- , NO_2^-) were measured using spectrophotometer techniques.

From the results of the chemical analyses, ionic strength (I), calcite saturation index (SIc), dolomite saturation index (SI_d), $r\text{Ca}^{2+}$, $r\text{Mg}^{2+}$, $r\text{Ca}^{2+}+r\text{Mg}^{2+}$, and $r\text{Ca}^{2+}/r\text{Mg}^{2+}$ ($r = \text{mg/l}$ of ion/equivalent weight of ion; equivalent weight of ion = atomic weight of ion/ valence of ion) were calculated (Garrels and Christ, 1965; Thrailkill, 1976). SIc and SI_d are defined as follows:

$$\text{SIc} = (\text{Ca}^{2+}) \cdot (\text{CO}_3^{2-}) / \text{Kc} \quad (1)$$

$$\text{SI}_d = (\text{Ca}^{2+}) \cdot (\text{Mg}^{2+}) \cdot (\text{CO}_3^{2-})_2 / \text{Kd} \quad (2)$$

Where the brackets indicate activities of the ions; Kc and Kd are the respective equilibrium constants of calcite = -8.48 and dolomite = -16.54, respectively.

Ionic strength (I) is then calculated. Once I is known, the activity of ions Ca^{2+} , Mg^{2+} and CO_3^{2-} are calculated using the Debye-Hückel equation (Garrels and Christ, 1965) as follows:

$$I = 1/2 \sum m_i z_i^2 \quad (3)$$

Where I is the ionic strength of the solution, the summation sign (\sum) means that the contributions from all ions in solution, m_i is the concentration of the ion and calculated the concentration of m_i in mole/L, and finally z_i is the charge on the particular ion.

The values of the equilibrium constants used in this study are those given by Langmuir (1971), Thrailkill (1976), and Drever (1983). The most important uncertainty among measured values is in the pH. The uncertainty of pH strongly depends on changes in experimental details and on the pH value itself. The uncertainty is the lowest near the isopotential point and in the center of the calibration line and can increase by a factor of 2 when moving from around pH 7 to around pH 2 or 11. Therefore, it

is necessary to estimate the uncertainty separately for each measurement. For routine pH measurement, the uncertainty cannot be significantly reduced by using more accurate standard solutions than ± 0.02 pH units; the uncertainty improvement is small. However, in routine pH determination this fundamental uncertainty (which in the case of the NBS scale amount to $\Delta\text{pH} = \pm 0.005$) will be negligible (Leito et al., 2002). The total uncertainty in calculated values of SIc and SI_d is about ± 0.15 units, uncertainty for SIc and SI_d are a measure of range of measurements from the average, also called deviation or error (Vern Lindberg, 2000).

Results and Discussion:

Water Quality: Parameters and Discharge

Statistical calculations were conducted using the statistical software packages SPSS version 15 for windows XP. Tables 1, 2, 3, and 4 showed the descriptive statistics (minimum, maximum, average, standard deviation, and coefficient of variation (Cv)) of the samples collected from the different springs and wells in the studied area.

Figures 5 and 6 showed the seasons of Al-Dhaher cave spring and the type of springs, respectively with the concentration values of pH, TDS, EC, T, Q, Cl^- , SO_4^{2-} , NO_3^- , HCO_3^- , K^+ , Na^+ , Mg^{2+} and Ca^{2+} .

In Tables 1, 2, 3, 4, 5 and 6 the essential values of statistical measures of pH, Cl^- , HCO_3^- , SO_4^{2-} and NO_3^- parameters are also given and discussion.

Many water quality parameters showed striking seasonal variations. Temperature and seasonal variation is relatively uniform during the time. There is also a variation in concentrations and discharge. There are different reasons for these variations. Some of them depend on discharge and seasonality; the magnitudes of the fluctuations in discharge are much greater than those of concentrations. The ratio of highest and lowest concentrations of cations and anions for water discharge is large (58.75:1) followed by K^+ (33.5:1) and Na^+ (19.1:1). There is low ratio for Cl^- (2:1), sulphate, SO_4^{2-} (1.84:1), NO_3^- (1.54:1), Mg^{2+} (1.39:1), Ca^{2+} (1.34:1), HCO_3^- (1.33:1), EC (1.21:1), TDS (1.21:1) and temperature, T (1.17:1). The dominant anion and cation in the water of Al-Dhaher springs is HCO_3^- and Ca^{2+} , respectively. The values of NO_3^- show may be anthropogenic influence but it is five times less than those in the Jordanian wells in which the medium level of NO_3^- is 33 mg/l (Obeidat et al., 2008).

Figure 7 shows the relation between temperature (T) and discharge (Q), while Figure 10 shows relation of water quality parameters and discharge at Al-Dhaher springs. The relations show that the data of the discharge (Q) with variables of T, Ca^{2+} , Mg^{2+} , $(\text{Ca}^{2+} + \text{Mg}^{2+})$, and HCO_3^- strong relation

from a strong distribution not only in skewness, but also by the number of the other values that may be far from the normality values. It is noted that only temperature is approaching around normal values. As presented in Figure 10, some outliers and extreme values for the variables of Ca^{2+} , Mg^{2+} , and HCO_3^- are recorded. The extreme values for these variables are due to carbonate aquifers, while the extreme values of other variables are unexpected and may be due to non-suitable measurements or due to the contamination of water samples from human disposals.

Seasonal Variation in the Water Quality

The importance of karst caves in the study area is to determine the types of rocks and their effect to dissolve in aqueous solutions, to study the most important geological structures that appear in the region and its relationship with the phenomenon of karstification (Dar et al., 2011), to study the characteristics of thermodynamics of groundwater and their impact on the karstification, and to study the effect of rainfall and runoff, and how effective they are in the formation of stalactite and stalagmites.

The amount of rainfall in the study area is limited to winter and is the only source of ground water recharge; seasonal variation could be noticed in the water quality of the different springs and wells.

Three types of variations were noticed during this study between the water quality of the samples collected in winter and those collected in summer. Winter samples are slightly diluted than those collected in summer (Figs. 5 and 6) and have slightly lower concentrations of cations: Ca^{2+} , Mg^{2+} , Na^+ , K^+ and anions: HCO_3^- , Cl^- , NO_3^- , SO_4^{2-} . This is may be due to the rainfall, infiltration and ground water recharge during winter. While during samples analyses taken along channel of stream from upstream to downstream increase was found in the Na^+ and Cl^- caused by evaporation and thus decreasing the discharge of water gradually until it dries up completely.

The plot figures (Figs. 7, 8, 9, 10, 11) and the results of the distribution for normality showed almost a normal distribution at all seasons for all parameters analyses. Samples were collected in two different seasons, summer and winter; therefore, it was very important to check whether there are significant differences in the mean concentrations of the different parameters between the two seasons.

Mann-Whitney test showed no significant differences between the mean concentrations of all of the studied parameters except the temperature and ions of Na^+ and K^+ . Based on this result, the available data of all springs and wells will be averaged regardless the season for further statistical analysis.

Physical and chemical analyses (Tables 1, 2, 3, and 4) for all types of water samples (Al-Dhaher Cave Spring, Ain Zubia, Ain Zgaeg, and wells), as well as the calculated indexes of saturation of calcite (SIc) and of dolomite (SI_d) and some of the calculated ion ratios. Tables 1, 2, 3, and 4 also show the average calculated values of the different chemical parameters, their minimum, maximum, average, standard deviation (σ_x) and the value of the coefficient of variation (Cv%), where the coefficient of variation (Cv) = $(\sigma_x / \text{average}) * 100$. While, the same procedures and equations were used to calculate the data and get the results, at many different studies and interpretations in many researches, as Garrels and Christ, 1965; Langmuir 1971; Thraillkill, 1976; Drever 1983; Dreybrodt and Gabrovšek, 2003.

These results confirm the data on the nature of Al-Dhaher Cave Spring karst structure and the groundwater flow regime obtained by other methods of exploration (e.g. Abu-Jaber et al. 2006; Obeidat et al. 2008). It was found that inflow of the input water types of rainwater enhance the dissolutive process of the aquifer system.

pH and Temperature of Ground Water

pH and Temperature of water samples were determined in the field. Small changes in pH (0.3 units or even less) are usually associated with relatively large changes in other water qualities. Most natural waters will have pH values from pH 5.0 to pH 8.5. The acidic, freshly fallen rainwater may have a pH value about 5.5 to 6.0. If it reacts with soils and minerals containing weak alkaline materials, the hydrogen ion concentration will decrease. The water may become slightly alkaline with a pH of 8.0-8.5. Sudden changes in pH values serve as warning signals that water quality may be adversely affected through the introduction of contaminants.

Correlation coefficient and regression analysis for figures (Fig. 7) of curve fitting. These procedures are used for looking at the relationship between different factors, and for graphing the results in statistically meaningful ways.

There is a three stages procedure:

Plot the results on graph paper, as a result of SPSS program, and does the relationship look (or is expected to be) linear, or is it logarithmic, or sigmoid (S-shaped).

Calculate the correlation coefficient, and how close the fit is, in statistical terms .

If the correlation coefficient is significant, and other conditions are met, proceed to regression analysis, which gives the equation for the line of best fit.

The pH values of all types of groundwater are relatively stable (pH: 7.19) with a standard

deviation of 0.22 (Table 5), while pH values are: 7.05-7.44 in the Al-Dhaher Cave Spring, 6.78-7.14 in the Ain Zubia, 6.77-7.7 in the Ain Zgaeg, and 7.14-7.9 in the wells, with standard deviations of 0.166, 0.101, 0.26, and 0.233 respectively (Tables 1, 2, 3, 4).

Several factors affect the value of pH: source of the water, rainfall, water temperature, geology, soil and discharge. Due to a moderately affected all that are factors in the water of Al -Dhaher Cave Spring, the value of pH for all water samples were arranged around normal pH (7). Generally, pH value was decreased through the recharge is higher during the low temperature season (winter), while it is increased through the recharge is lower during the higher temperature season (summer).

Temperature value varied from 14.3 to 16.68° C with average of 15.25° C (Table 5) reflecting the wide range of the temperature of the infiltrating recharge water (Tables 1, 2, 3, 4, 5). We note a strong correlation between temperature of the springs and discharge $r = 0.97$ (Al-Dhaher Cave Spring), 0.83 (Ain Zubia), 0.80 (Ain Zgaeg), and 0.81 (wells) (Fig. 7), which express the relation of the recharge to the climate seasons.

Total Dissolved Solids (TDS)

Total dissolved solids (TDS) comprise inorganic salts, such as calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulfates, and some small amounts of organic matter that are dissolved in water. The TDS concentration is a secondary drinking-water standard and is regulated because of its esthetic effect rather than a health hazard. Elevated TDS indicate that the dissolved ions may cause the water to be corrosive, of salty or brackish taste, resulting in scale formation.

As presented in Tables 1, 2, 3, and 4 all the collected water samples of springs and wells are fresh water type according to Carroll (1962) classification, with TDS values of 438-515 mg/l in the Al-Dhaher Cave Spring, 455-689 mg/l in the Ain Zubia, 408-692 mg/l in the Ain Zgaeg, and 428-586 mg/l in the wells water. Furthermore, higher values were recorded only in summer seasons in all water types.

The reason for this result is due to the decrease of surface rainwater into recharge of groundwater in the area, as well as in the case of groundwater depletion through irregular withdrawals of wells in the area and use in drinking.

Whenever, during the shortage supply season of surface water to the groundwater and withdrawn high amount of water to domestic homes, the final result are falling level of groundwater, and this works on the increase of the concentration ratio of the mass of dissolved solids in the water, which works to reduce water quality and increasing salinity as a final

result, and transition from suitable drinking fresh water to not suitable salt water.

Electrical Conductivity (EC)

The electrical conductivity (EC) of water is a measure of the total salt content of water based on the flow of electrical current through the sample. The higher the salt content the greater the flow of electrical current.

The electrical conductivity of the water depends on the water temperature: the higher the temperature, the higher the electrical conductivity would be. The electrical conductivity of water increases by 2-3% for an increase of 1 degree Celsius of water temperature (Smart, Growing Intelligently, 2012).

Since the electrical conductivity is a measure to the capacity of water to conduct electrical current, it is directly related to the concentration of salts dissolved in water, and therefore to the Total Dissolved Solids (TDS). Salts dissolve into positively charged ions and negatively charged ions, which conduct electricity. Since it is difficult to measure TDS in the field, the electrical conductivity of the water is used as a measure. EC for drinking water can be converted to TDS using the following calculation (<http://www.lenntech.com/applications/ultrapure/cond-uctivity/water-conductivity.htm#ixzz2E4EaXuDf>, 2012):

$$\text{TDS (mg/l) or (ppm)} = 0.5 \times \text{EC (dS/m or mmho/cm)} \text{ or } = 0.5 * 1000 \times \text{EC } (\mu\text{S/cm})$$

The electrical conductivity (EC) for all water samples varied from: 685 to 1162 $\mu\text{S/cm}$ reflecting the different amounts of the total dissolved ions in water.

The measurements conducted during this study showed that the EC values ranged between 736-865 $\mu\text{S/cm}$ in the Al-Dhaher Cave Spring (Table 1), 764-1157 $\mu\text{S/cm}$ in the Ain Zubia (Table 2), 685-1162 $\mu\text{S/cm}$ in the Ain Zgaeg (Table 3), while in the wells the values ranged between 719-984 $\mu\text{S/cm}$ (Table 4). The highest values of EC in the springs and wells were recorded in summer seasons.

Tables 2, 3 and 4 show that the values of electrical conductivity (EC) for springs samples is low, and lie within the concentration level of standard drinking water. The EC values have less than value of seawater about fifty times (Suttar, 1990), and attributed this to the low of the Total Dissolved Solid in the spring's water in the study region, making it safe to drink. Except for some dissolved of Ca^{2+} , Mg^{2+} and HCO_3^- ions and granted by the relatively high value of the electrical conductivity, and due to the fact that water springs in the study area and in particular Al-Dhaher spring pass through the limestone and considered its aquifer.

Since the EC and TDS are measurements of the total salt content, they must be directly proportional. The correlation between these two parameters for the analyzed samples in this study was plotted in Figure 8 which showed a very strong linear correlation ($r = 1$) with a mathematical approximation of ($\text{TDS mg/l} = 0.55 \text{ EC } \mu\text{S/cm}$).

Chemical Relations of Major Dissolved Ions

Rainwater, as it passes through the air, through, and over the land, dissolves many chemical species. A wide range of different elements (e.g.: nitrogen, oxygen and carbon dioxide) can become dissolved in groundwater as a result of interactions with the atmosphere (Earle and Krogh, 2004; DHV, BV et al., 2002; Dreybrodt and Gabrovšek, 2003; Kempe et al., 2009), the surficial environment, soil and bedrock. The fact that it dissolves carbon dioxide from the air is important because when carbon dioxide is present in water, it forms carbonic acid and this acid enhances water's ability to dissolve chemical species (salts) contained in rocks and soil. In passing through polluted atmosphere, it is also possible for the water to dissolve gases associated with pollution such as sulphur and nitrogen oxides. Some of these gases can also make the water acidic, further adding to the water's ability to dissolve salts (DHV, BV et al., 2002).

By the time, that rainwater has passed over and through land to become groundwater or surface water, it has normally acquired many dissolved chemical species. Groundwater's tend to have much higher concentrations of most constituents than do surface waters, and deep groundwater's that have been in contact with rock for a long time tend to have higher concentrations than shallow and or young waters (Earle and Krogh, 2004). Clearly, the precise chemical composition of the water will depend upon the types of rock and soils with which the water has been in contact and this can be used to characterize a particular water by determining its chemical makeup. Tables 1, 2, 3 and 4 show the concentration of major ions in water of different springs at the different seasons in the study area, while Table 5 shows the mean of the major ion concentration in the same springs.

All analyzed samples are classified as calcium bicarbonate water. Ionic equivalent abundances show that cations $\text{Ca}^{2+} > \text{Mg}^{2+} > (\text{Na}^+ + \text{K}^+)$ and for anions $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$ dominate. Calcium and bicarbonate account for approximately 80% of the total ions. NO_3^- and SO_4^{2-} account for only about 6 to 9% of the total ions in any given analyses. Most abundant ions HCO_3^- and Ca^{2+} have also greater standard deviation (39 and 11.2, respectively), which indicates larger range of their

values, while Mg^{2+} cations have also smaller standard deviation of 3.7, which indicates smaller range of their values (Table 5).

Correlations of concentrations between Ca^{2+} and Mg^{2+} with HCO_3^- were very strong but that of Ca^{2+} ($r = 0.98$ Al-Dhaher Cave Spring, 0.90 Ain Zubia, 0.90 Ain Zgaeg, and 0.94 wells water) were stronger than that of Mg^{2+} ($r = 0.96$ Al-Dhaher Cave Spring, 0.82 Ain Zubia, 0.87 Ain Zgaeg, and 0.70 wells water) (Fig. 9). Certainly, the main reason is the strength of the correlation and the chemical relation between Ca^{2+} with HCO_3^- , which is stronger than the correlation strength between Mg^{2+} with HCO_3^- .

A plot of equivalent concentrations of Ca^{2+} to HCO_3^- shows that Ca^{2+} balances HCO_3^- on a nearly one-for-one equivalent basis, and the Y-intercept is near zero. Correlation between the sum of equivalents ($r\text{Ca}^{2+} + r\text{Mg}^{2+}$) and HCO_3^- is even very strong ($r = 0.98$ Al-Dhaher Cave Spring, 0.92 Ain Zubia, 0.92 Ain Zgaeg, and 0.93 wells water) (Figure 9). Moderate to low correlations have been found between some of other ions like Cl^- , NO_3^- , SO_4^{2-} and HCO_3^- , while that with Ca^{2+} and Mg^{2+} was very small and usually $r < 0.1$.

The concentration value of Ca^{2+} normal was below 15mg/l, although this can be above 100 mg/L where water is associated with aquifer of carbonate-rich rocks. Mg^{2+} concentrations were between 1 to 50 mg/L depending upon the rock type within the aquifer (DHV, BV et al., 2002).

Calcium and magnesium, when combined with bicarbonate, carbonate, sulphate (Kempe et al., 2009) and other species, contribute to the hardness of natural waters resulted on deposited scale when such waters are heated.

The concentration of carbonates and bicarbonates in water has a major effect on both the hardness and the alkalinity of water. The relative amounts of carbonate, bicarbonate and carbonic acid in water is related to the pH. Under normal surface water pH conditions (i.e., less than $\text{pH} = 9$), bicarbonate predominates. Bicarbonate concentrations in natural waters range from less than 25 mg/L in areas of non-carbonate rocks to over 400 mg/L where carbonate rocks are present (DHV, BV et al., 2002).

In waters springs where the bicarbonate content is high, there is a tendency for calcium and magnesium to precipitate out as carbonates. As water is originated in marl, marly limestone, and limestone rocks, the total hardness is moderate to high, and the average value is nearly 355 mg/L, also the SO_4^{2-} concentration is low; the average value is 15.35 mg/L (Table 5).

Sulphate is present in all surface waters as it arises from rocks, which contains a high sulphate concentration. In addition to its role as a plant

nutrient, high concentrations of sulphate can be problematic as they make the water corrosive to building materials and are capable of being reduced to hydrogen sulphide when zero dissolved oxygen conditions prevail in the water body (Kempe et al., 2009). Normally, sulphate concentrations in surface waters are between 2 and 80 mg/L although they may exceed 1000 mg/L if industrial discharges or sulphate-rich minerals are present (DHV, BV et al., 2002). The WHO (1993) guideline value for sulphate in drinking water is 400 mg/L.

All natural waters contain sodium ions (Na^+) as the element is one of the most abundant on the planet. High concentrations in ground waters, however, are normally associated with pollution from industrial discharges or sewage effluent or from dissolved of salt rocks, clays, or plagioclase intrusions. Normally, sodium concentrations in drinking water are below 200 mg/L depends on World Health Organization guideline limit.

Potassium ions are highly soluble and are essential for most forms of life. Potassium in the water environment is readily taken up by aquatic life, therefore (DHV, BV et al., 2002). The concentration of potassium ions (K^+) in natural fresh waters is generally low (normally less than 10 mg/L).

Chlorides in fresh waters generally come from rocks, the sewage, agricultural and industrial effluents. Fresh water concentrations of chloride are normally less than 40 mg/L and can be as low as 2 mg/L in waters, which have not been subject to pollution. Chloride concentrations over 100 mg/L give the water a salty taste and thereby make it unsuitable for drinking by humans or animals.

Though nitrate (NO_3^-) is listed as a major ion, moderately concentrations of nitrate average 20.34 mg/L (Table 5) have been reported from all springs in the study area where municipal wastewater from the countries over the aquifer has contaminated the groundwater. Excessive amount of nitrate in drinking water causes methaemoglobinaemia in bottle-fed infants (DHV, BV et al., 2002). WHO (1993) has recommended a guideline value of 10 mg NO_3^- N/L.

The moderately values for nitrate are observed for springs overlain by villages lacking a proper sewer system. There is a statistically significant correlation between nitrate concentration in spring water and the number of cesspools in the catchment area of each spring (Obeidat et al., 2008). This indicates that domestic wastewater form the major source of nitrate in the spring water. The time that the cesspools could take to contaminate the groundwater can vary depending on the depth to water table, degree of fracturing and karstification of the aquifer, and permeability of the aquifer (Gregory et al., 2001; Kiraly, 2003; Aloui and Chaabani, 2007).

Other potential sources of groundwater pollution include agricultural activities (fertilizers and animal husbandry, olive presses). The spatial variation in nitrate concentration can be attributed to different factors, such as hydrogeology, degree of karstification, and land use (Obeidat et al., 2008).

$\text{rCa}^{2+}/\text{rMg}^{2+}$ ratio in groundwater has a clear geochemical implication; their values are usually lower in dolomite and higher in limestone or marl (Langmuir, 1971; Zotl, 1974; Eftimi and Benderev, 2007). The mean $\text{rCa}^{2+}/\text{rMg}^{2+}$ ratio for some springs in pure limestone of Albania is 11.8 and for some other dolomite springs is 2.1 (Eftimi, 2005) and for Iskrets spring is 3.3 (Eftimi and Benderev, 2007). The $\text{rCa}^{2+}/\text{rMg}^{2+}$ ratio for all springs in the study area is 1.92 (Table 5), while this ratio for all springs showed that the average values are: 1.54 in the Al-Dhaher Cave Spring, 2.49 in the Ain Zubia, 1.76 in the Ain Zgaeg, while in the wells the values average is 1.91, which suggest that water moves in limestone or that marly limestone is rich with dolomite.

Between $\text{rCa}^{2+}/\text{rMg}^{2+}$ ratios and the sums of $\text{rCa}^{2+} + \text{rMg}^{2+}$, an indirect correlation exists, that is related to the higher solubility of the limestone than that of dolomite (Eftimi and Benderev, 2007). As presented in Figure 9, correlation of sums of equivalent ($\text{rCa}^{2+} + \text{rMg}^{2+}$) to ($\text{rCa}^{2+}/\text{rMg}^{2+}$) ratio varies from very strong to very weak ($r = 0.98$ Al-Dhaher Cave Spring, 0.74 Ain Zubia, 0.44 Ain Zgaeg, and 0.80 wells water).

These important data showing the aquifer source of spring water in the study area and the type of ground layers preserved of water, where the strength of the relationship between Ca^{2+} and Mg^{2+} ions absolutely demonstrates that source springs water coming out of the ground are carbonate rocks; limestone rich in Ca^{2+} and Dolomite rich in Mg^{2+} .

Water Chemistry and Discharge

Based on water chemistry of springs there are two basic types possible that response to discharge according to Jacobson and Langmuir (1974). The first is the response controlled mainly by discharge and independent of the time of year. The second is the response controlled by the season and largely independent of the discharge. In the following, the quality variables of Al-Dhaher Cave Spring are controlled mostly by different seasons more than discharge.

Correlations of Ca^{2+} , Mg^{2+} , ($\text{Ca}^{2+} + \text{Mg}^{2+}$), and HCO_3^- to discharge (Q) of all springs and wells samples vary from very strong ($r = 0.95, 0.96, 0.96, 0.90$ respectively) with Al-Dhaher Cave Spring (Fig. 10), to moderately strong ($r = 0.69, 0.71, 0.70, 0.87$) with Ain Zubia, ($r = 0.81, 0.63, 0.79, 0.80$) with Ain Zgaeg, and ($r = 0.91, 0.57, 0.90, 0.86$) with wells

water. While correlations were very low to no correlation of the other ions like Cl^- , NO_3^- , and SO_4^{2-} with discharge (Q) and usually $r < 0.3$.

Chemical Equilibrium and Saturation Indices

The quality of the recharge water and its interactions with soil and rocks during its percolation and its storage in the aquifers are key factors in the chemistry of ground water. These interactions involve mainly dissolution and precipitation processes, which are controlled by the solubility products of the different involved mineral phases (Drogue, 1992). Generally, the saturation indices (SI) are used to express the tendency of water towards precipitation or dissolution. SI of the collected samples were calculated for the major mineral phases using the software package (PHREEQC for windows XP) according to Parkhurst and Appelo, (2001).

Calcite (limestone), marly limestone, and dolomite represent the major rocks that built-up the geology of the study area. According to tables 1, 2, 3, and 4 show that all the waters of the four clustering groups of springs and wells are supersaturated with respect to the main carbonate mineral (calcite and dolomite).

We noted also that the indexes of calcite (SIc) and dolomite (SID) saturation with the sum of ($\text{Ca}^{2+} + \text{Mg}^{2+}$) of Al-Dhaher Cave Spring and other springs have very strong correlation ($r = 1.0$, 1.0 to Al-Dhaher Cave Spring (Fig. 11), 0.95 , 0.92 to Ain Zubia, 0.97 , 0.96 to Ain Zgaeg, and 0.88 , 0.92 to wells water). While the correlation coefficients of the SIc and SID to discharge (Q) were very strong ($r = 0.97$, 0.96) to Al-Dhaher Cave Spring (Fig. 11), but for Ain Zubia, Ain Zgaeg, and wells water are also moderately strong ($r = (0.68, 0.67)$, $(0.77, 0.68)$, and $(0.73, 0.74)$, respectively). The saturation of the water with calcite and dolomite is higher during small discharges while it is smaller during large discharges of the springs, and this reflects the time duration of the contact of groundwater with the aquifer rocks (Eftimi and Benderev, 2007), and almost reflects the event season.

Our data indicate that the springs are undersaturated with respect to calcite and dolomite, but the amount of undersaturation with respect to dolomite is much greater than that with respect to calcite. This is explained by the high solution kinetics of calcite in comparison with dolomite (Thraillkill, 1977; Appelo and Postma, 1999; Eftimi and Benderev, 2007).

Physical Behaviors of the Karst Aquifers

There are at least two end member types of the groundwater flow in karst aquifers: conduit flow and diffuse flow. The variation of the physical and

chemical characteristics of the springs could be used to characterize physical behavior of the karst aquifers (Shuster and White, 1971; Jacobson and Langmuir, 1974; Kiraly, 2003; Aloui and Chaabani, 2007, Eftimi and Benderev, 2007), and this could be done having in sight also the limitations (Scanlon and Thraillkill, 1987). Changes in water chemistry may be described through the use of the coefficient of variation (Cv%). According to Eftimi and Benderev (2007), the coefficients of variation result was greater for the conduit flow springs and less for diffuse flow springs.

Table 6 showed coefficients of variation for some variables measured in Al-Dhaher Cave Spring, Ain Zubia, Ain Zgaeg, and wells water compared with some literature data of Rock Spring, Thomson Spring (Jacobson and Langmuir, 1974), and Iskrets Spring (Eftimi and Benderev, 2007). Coefficients of variations of the used physical and chemical parameters suggest that such springs are of conduit type, while wells water suggests a diffuse flow water type. The mountain runoff provides essential groundwater recharge component. The tracer tests in the studied region, the monitoring on the spring flow-rate fluctuation and their connection to climatic factors prove water fast movement along karst channels during spring time and prove essential influence over saturated zone during dry seasons, as well (Benderev, 1989).

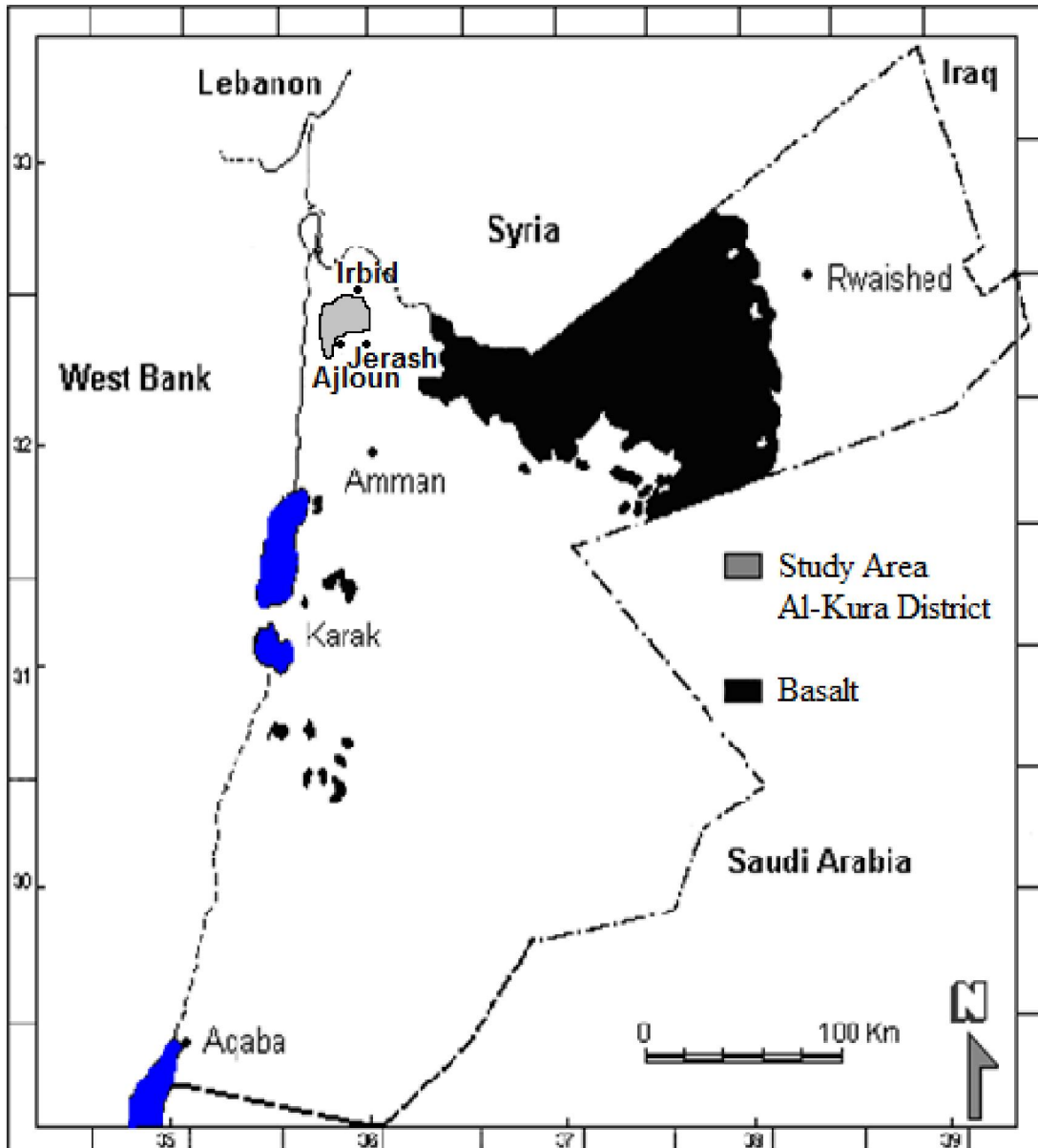


Figure 1a. Location map of the study area in Jordan.

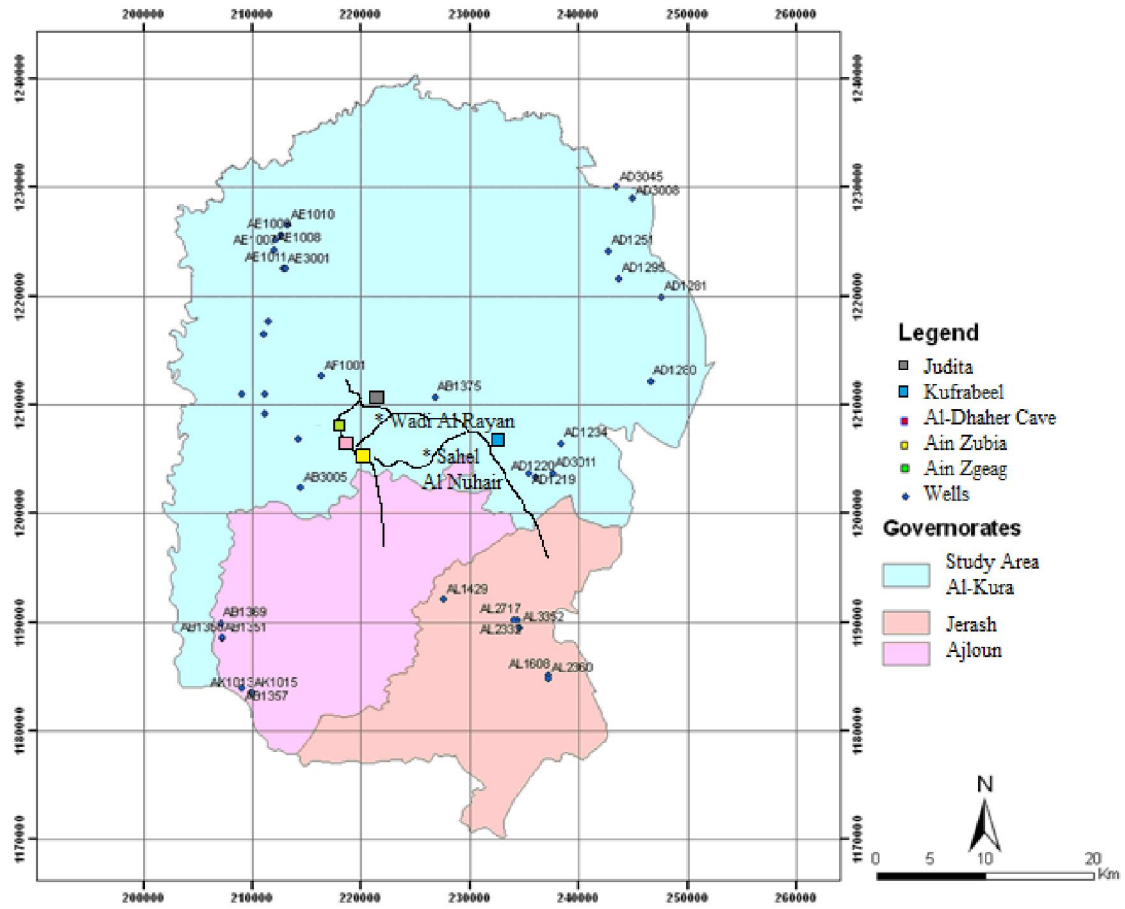


Figure 1b. Location map of Irbid governorate, Al-Kura District, springs, and wells of the study area.



Figure 2. Limestone rock shows fractures and joints at the surface over the cave area.



Figure 3. Stalagmite shape inside of Al-Dhaher Cave grow as a cylinder shape with length about two meters and about one meter diameter.



Figure 4. Curtain shape developed from carbonate water trickles down an inclined walls.

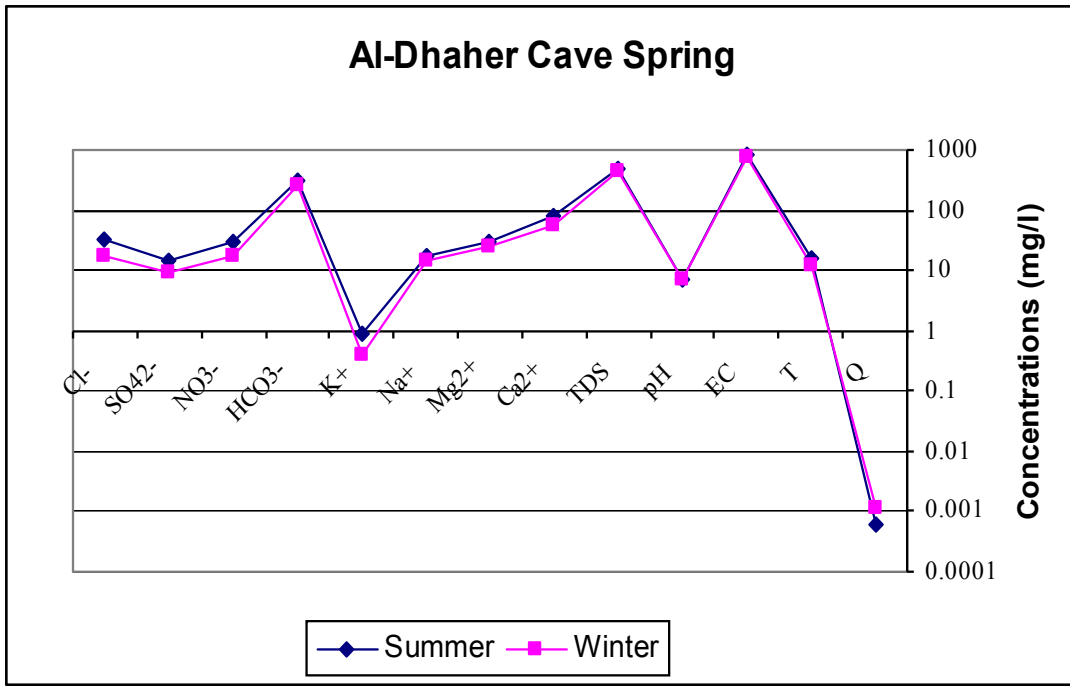


Figure 5. Plot of the samples collected in summer and winter from the Al-Dhaheer Cave Spring.

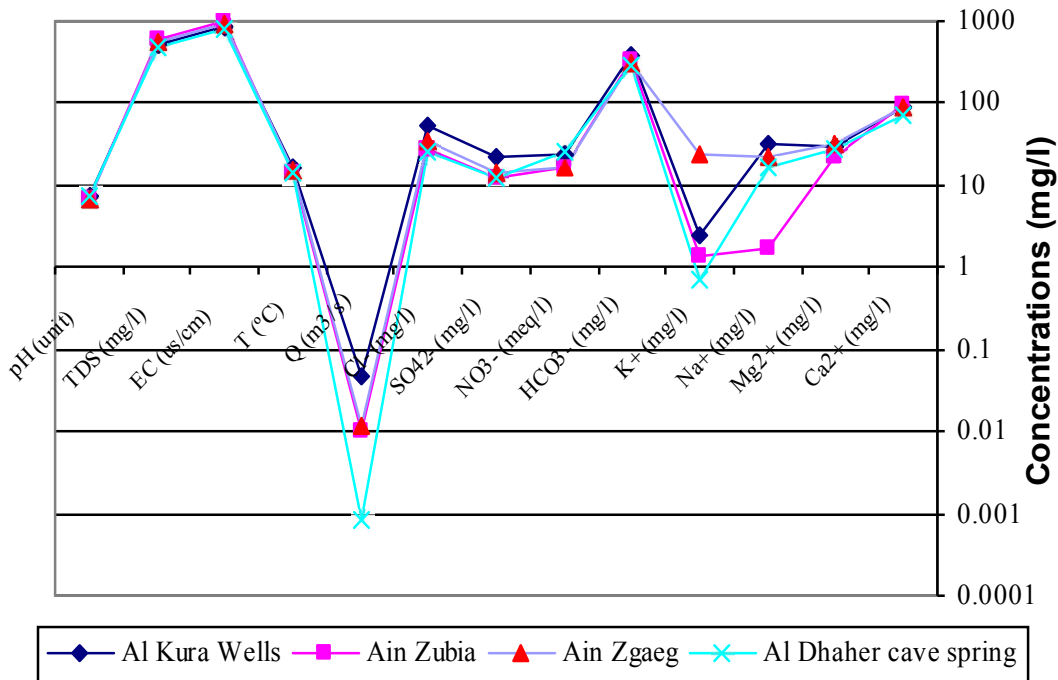


Figure 6. The comparison plot of the samples collected in summer and winter from the Al-Dhaheer Cave Spring, Ain Zubia, Ain Zgaeg, and Al-Kura wells water.

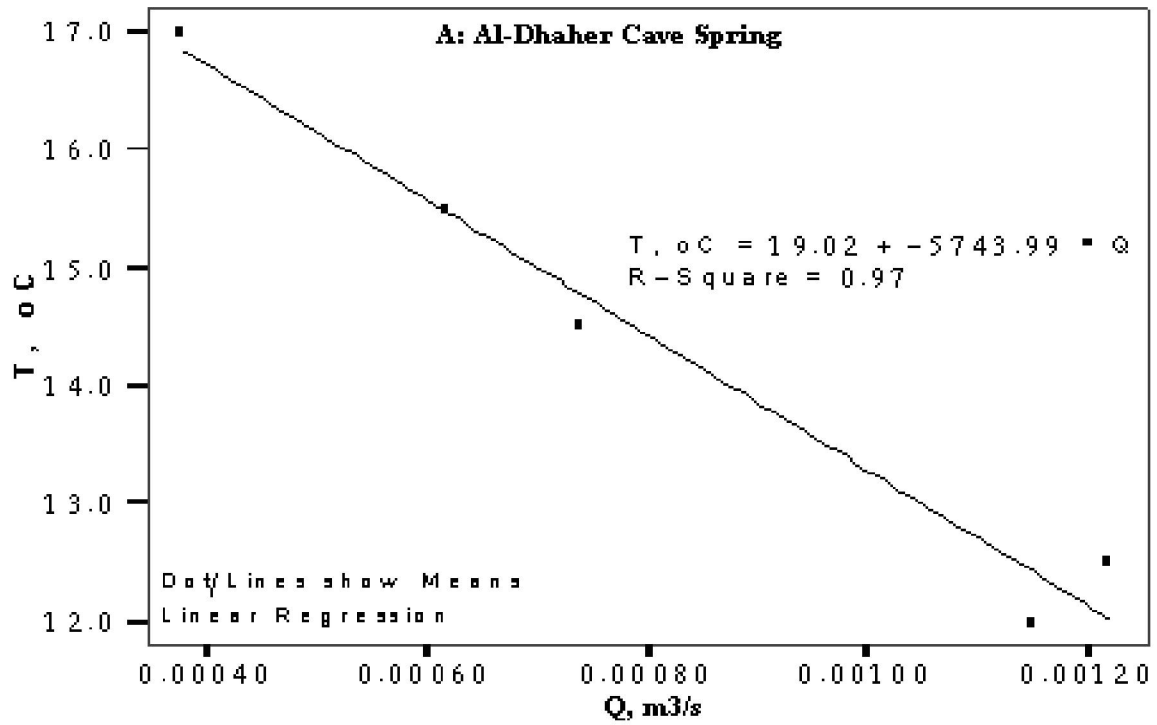


Figure 7. Relation between temperatures (T) of ground water with discharge (Q) to Al-Dhaher Cave Spring.

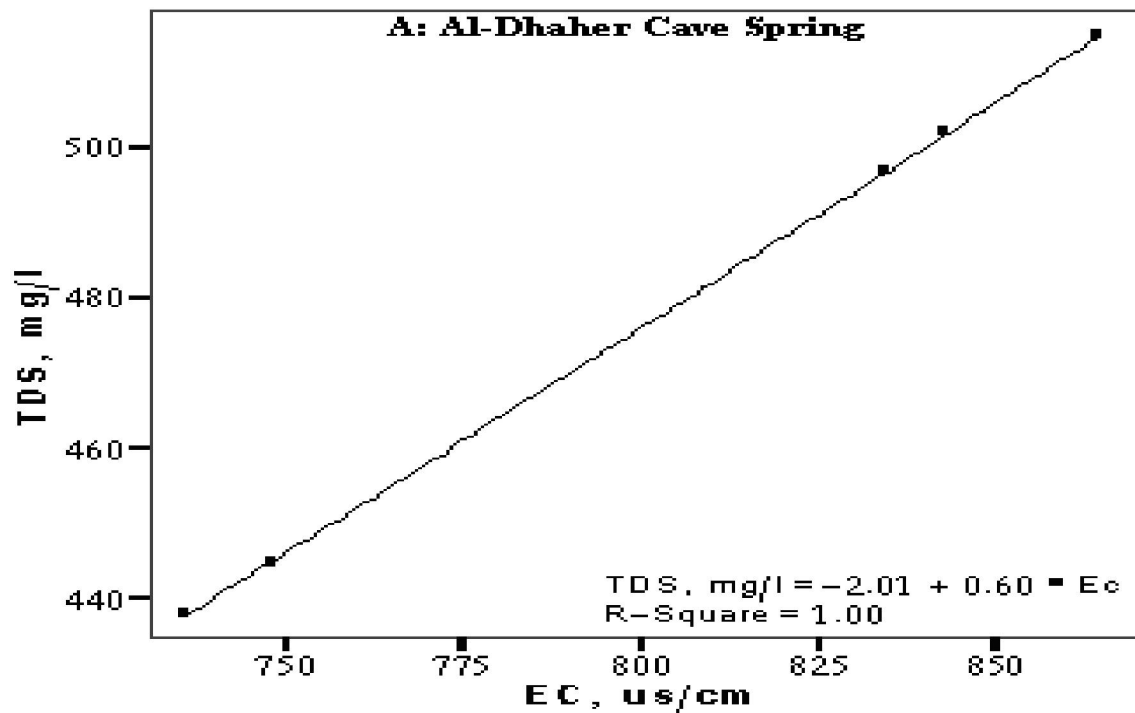


Figure 8. Relation between total dissolved solid (TDS) of ground water with electrical conductivity (EC) to Al-Dhaher Cave Spring.

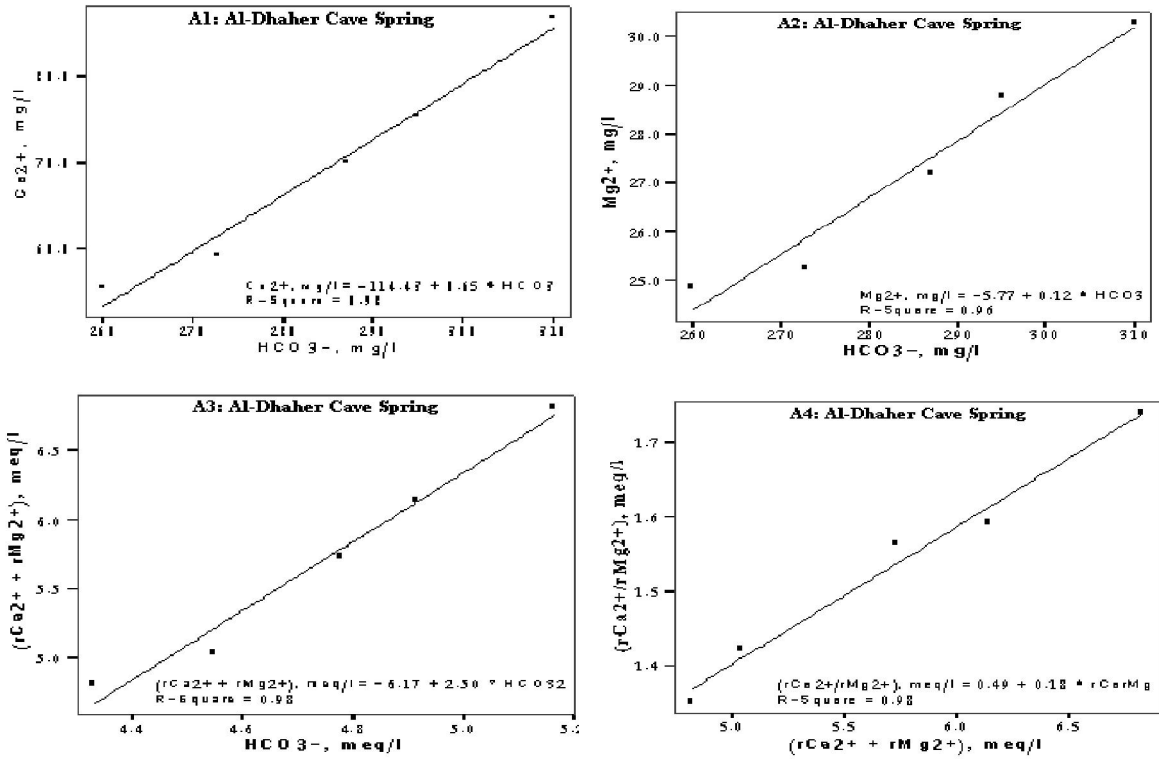


Figure 9. Relation between HCO_3^- and other major cations; (A1, A2, A3, A4) to Al-Dhaher Cave Spring.

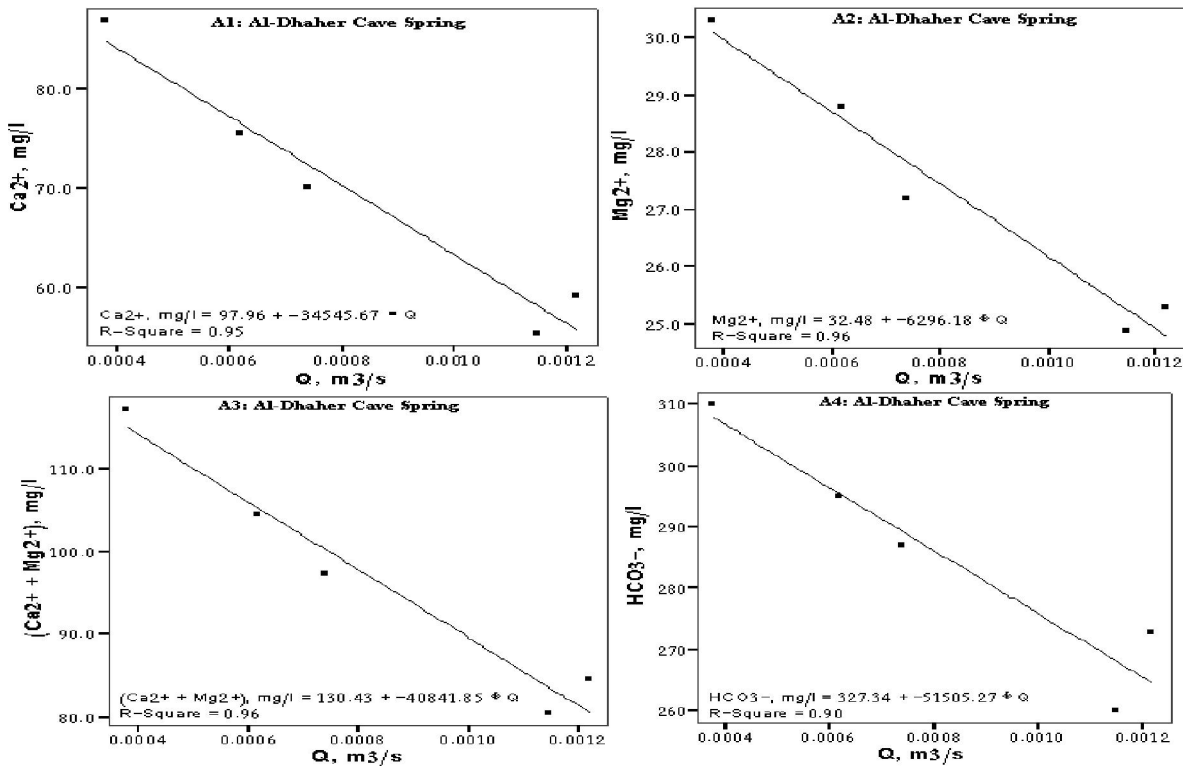


Figure 10. Relation between discharge (Q) and other major ions; (A1, A2, A3, A4) to Al-Dhaher Cave Spring.

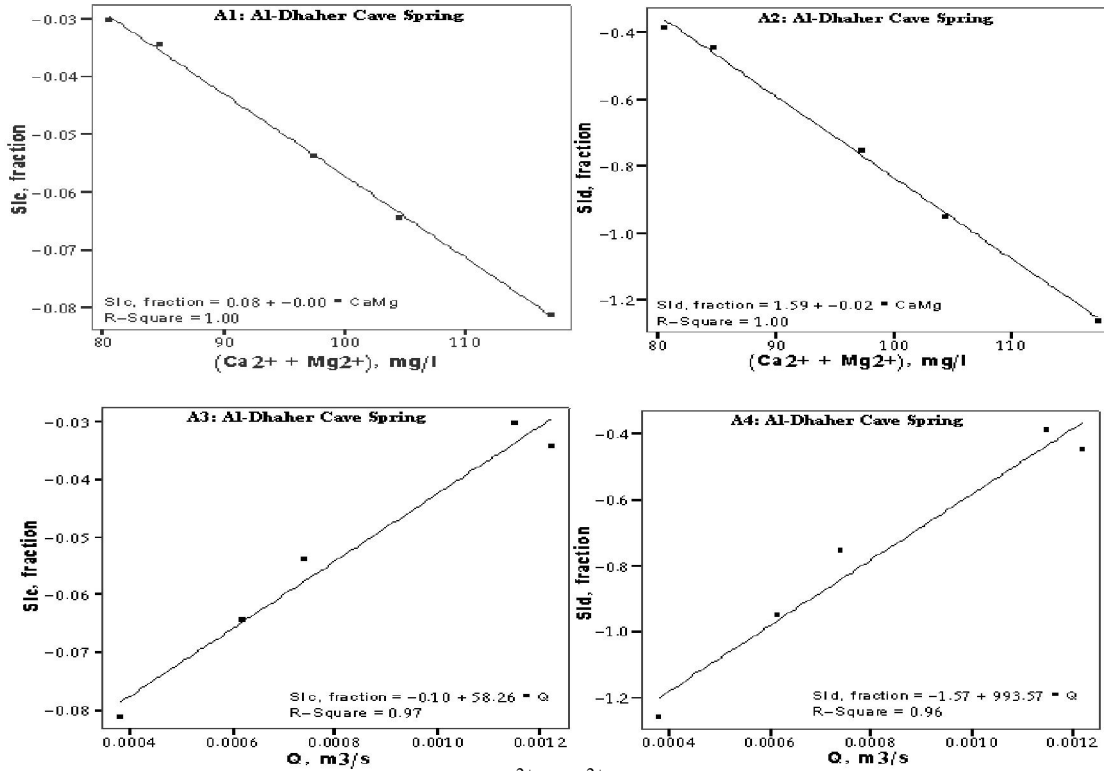


Figure 11. Relation between SI_c and SI_d versus of $(Ca^{2+}+Mg^{2+})$ and discharge (Q), (A1, A2, A3, A4) to Al-Dhaher Cave Spring.

Table 1. Physical and chemical analyses and statistical parameters of the Al-Dhaher Cave Spring.

Spring Name	Q, m ³ /s	T, °C	EC, us/cm	pH, unit	TDS, mg/l	Ca ²⁺ , mg/l	Mg ²⁺ , mg/l	Na ⁺ , mg/l	K ⁺ , mg/l	Na+K, mg/l	rCa ²⁺ +rMg ²⁺ , meq/l	rCa ²⁺ /rMg ²⁺	SI _c	SI _d	HCO ₃ ⁻ , mg/l	NO ₃ ⁻ , mg/l	SO ₄ ²⁻ , mg/l	Cl ⁻ , mg/l
Al Dhaher Cave Spring	0.00074	14.5	835	7.2	497	70.2	27.2	16.2	0.84	17.04	5.741	1.565	-0.054	-0.75	287	28.5	11.5	21.0
	0.00115	12	748	7.05	445	55.6	24.9	15	0.45	15.45	4.823	1.354	-0.0035	-0.385	260	16.7	8.8	15.1
	0.00062	15.5	843	7.32	502	75.7	28.8	18.6	0.95	19.55	6.147	1.594	0.064	0.949	295	30.1	14.1	35.0
	0.00122	12.5	736	7.07	438	59.4	25.3	15.3	0.31	15.61	5.046	1.424	0.034	0.445	273	18.9	9.7	18.4
	0.00038	17	865	7.44	515	86.9	30.3	19.2	0.98	20.18	6.829	1.739	0.081	1.258	310	32.3	16.5	38.4
Minimum	0.00038	12	736	7.05	438	55.6	24.9	15	0.31	15.45	4.823	1.354	0.081	1.258	260	16.7	8.8	15.1
Maximum	0.00122	17	865	7.44	515	86.9	30.3	19.2	0.98	20.18	6.829	1.739	-0.035	0.385	310	32.3	16.5	38.4
Average	0.00082	14.3	805.4	7.216	479.4	69.56	27.3	16.86	0.71	17.6	5.717	1.535	0.053	0.758	285	25.3	12.12	25.58
Σx	0.00036	2.08	59.06	0.166	35.34	12.62	2.29	1.92	0.31	2.2	0.817	0.151	0.021	0.362	19.35	7.02	3.17	10.43
Cv	0.43392	0.145	0.073	0.023	0.074	0.181	0.084	0.114	0.434	0.125	0.143	0.099	-0.47	0.477	8.8	0.068	0.272	0.268
Cv%	43.3924	14.5	7.33	2.3	7.4	18.1	8.4	11.4	43.4	12.5	14.3	9.9	-40	-47.7	6.8	27.75	26.2	40.8

- * $rCa^{2+}(\text{meq/l}) = \text{meq/l of } Ca^{2+} = (\text{mg/l of } Ca^{2+})/\text{equivalent weight of } Ca^{2+}$
- * equivalent weight of $Ca^{2+} = \text{atomic weight of } Ca^{2+} / \text{valence of } Ca^{2+} = 40.08/2 = 20.04$
- * equivalent weight of $Mg^{2+} = \text{atomic weight of } Mg^{2+} / \text{valence of } Mg^{2+} = 24.305/2 = 12.1525$
- * Saturation Index: $SI_c = (Ca^{2+}) (CO_3^{2-}) / K_c$
- * Saturation Index: $SI_d = (Ca^{2+}) (Mg^{2+}) (CO_3^{2-}) / K_d$
- * Coefficient of variation (Cv) = $\sigma x / \text{average}$
- * $Cv\% = 100 \sigma x / \text{average}$

Table 2. Physical and chemical analyses and statistical parameters of the Ain Zubia spring.

Spring Name	Q m ³ /s	T °C	EC us/cm	pH unit	TDS mg/l	Ca ²⁺ mg/l	Mg ²⁺ mg/l	Na ⁺ mg/l	K ⁺ mg/l	Na ⁺ +K ⁺ Mg/l	rCa ²⁺ /rMg ²⁺ meq/l	rCa ²⁺ /rMg ²⁺	SL _L	SL _H	HCO ₃ ⁻ mg/l	NO ₃ ⁻ mg/l	SO ₄ ²⁻ mg/l	Cl ⁻ mg/l
Ain Zubia	0.0085	15	1050	7.03	625	85.4	20.4	16.91	0.92	17.83	5.94	2.539	-0.069	0.716	311	7.5	2.4	22.3
	0.008	16	1062	7.03	632	92.7	21.2	18.8	1.21	20.01	6.37	2.652	0.105	1.141	338	7.5	4.3	34.1
	0.007	17	1105	7.14	658	103.2	25.4	21.2	1.52	22.72	7.24	2.464	-0.14	1.823	380	7.6	7.8	21.3
	0.0092	13	986	6.87	587	109.3	24.2	26.1	1.01	27.11	7.446	2.739	-0.123	1.519	392	8.8	1.9	37.1
	0.0135	11	776	6.87	462	59.7	18.4	12.9	0.03	12.93	4.493	1.968	0.032	0.299	220	8.8	1.1	37.1
	0.013	11.5	872	7.02	519	61.2	19.3	15.3	0.08	15.38	4.642	1.923	0.044	0.436	229	12.2	35.1	37.7
	0.0088	16.5	1026	7	611	99.8	22.5	22.1	2.03	24.13	6.832	2.69	0.119	1.371	352	23.8	32.1	33.5
	0.007	17.5	1157	7.06	689	112.2	26.7	28.89	2.32	31.21	7.796	2.548	0.148	-2.03	378	1.89	8.3	30.8
	0.0086	13.5	879	6.78	523	116.7	24.6	33.89	2.39	36.28	7.848	2.877	-0.15	1.892	392	22.1	8.0	29.8
	0.0125	10.5	842	6.8	501	98.4	20.5	22.98	1.29	24.27	6.597	2.911	-0.103	1.085	291	14.8	7.9	34.5
	0.015	10.5	764	6.95	455	62.9	19.1	13.89	0.12	14.01	4.71	1.997	-0.04	0.392	187	26.1	15.1	20.1
	0.013	12.5	853	7.01	508	68.5	20.1	19.1	0.15	19.25	5.072	2.067	-0.048	0.491	218	23.1	33.2	17.3
	0.0077	17.5	1084	7.03	645	97.2	23.5	29.78	1.73	31.51	6.784	2.508	0.107	1.284	357	31.9	21.1	15.2
	0.0075	18	1072	7.01	638	106.9	25.8	33.9	2.23	36.13	7.457	2.513	0.158	2.084	387	22.1	2.1	14.9
	0.0073	18.5	1117	7.02	665	125.3	26.3	38.8	2.81	41.61	8.417	2.889	0.195	-2.63	401	31.1	2.2	16.6
	Minimum	0.007	10.5	764	6.78	455	59.7	18.4	12.9	0.03	12.93	4.49	1.93	-0.2	-2.63	187	1.89	1.1
Maximum	0.015	18.5	1157	7.14	689	125.3	26.7	38.8	2.81	41.61	8.42	2.91	0.032	-0.3	401	31.9	35.1	37.7
Average	0.0098	14.57	976.3	6.97	581.2	93.29	22.53	23.64	1.323	24.96	6.51	2.49	-0.11	-1.3	322	16.62	12.173	26.82
Σx	0.0028	2.92	132	0.101	78.58	21.23	2.86	7.97	0.93	8.81	1.28	0.34	0.05	0.72	74.8	9.623	12.28	8.78
Cv	0.284	0.201	0.135	0.014	0.135	0.23	0.13	0.34	0.71	0.35	0.196	0.138	-0.47	-0.56	0.23	0.58	1.01	0.327
Cv%	28.4	20.1	13.5	1.4	13.5	22.76	12.67	33.72	70.53	35.31	19.6	13.76	-47.1	-56.15	23.2	57.9	100.84	32.7

Table 3. Physical and chemical analyses and statistical parameters of the Ain Zgaeg spring.

Spring Name	Q m ³ /s	T °C	EC us/cm	pH unit	TDS mg/l	Ca ²⁺ mg/l	Mg ²⁺ mg/l	Na ⁺ mg/l	K ⁺ mg/l	Na ⁺ +K ⁺ mg/l	rCa ²⁺ /rMg ²⁺ meq/l	rCa ²⁺ /rMg ²⁺	SL _L	SL _H	HCO ₃ ⁻ mg/l	NO ₃ ⁻ mg/l	SO ₄ ²⁻ mg/l	Cl ⁻ mg/l
Ain Zgaeg	0.01	14	995	6.96	592	88.4	30.2	16.88	1.84	18.72	6.896	1.775	-0.074	1.146	300	22.1	1.3	19.0
	0.009	17	1016	6.96	605	93.4	30.9	18.0	1.85	19.85	7.203	1.833	0.084	1.326	310	22.8	31.1	23.4
	0.008	19	1112	7.16	662	121.4	35.7	25.6	2.45	28.05	8.996	2.062	-0.14	2.568	355	16.3	6.7	22.2
	0.012	13.5	1162	6.9	692	106.4	38.8	30.3	1.11	31.41	8.502	1.663	0.128	2.546	351	14.7	18.7	43.1
	0.018	12	706	6.9	420	59.9	22.3	11.2	0.73	11.93	4.824	1.629	0.023	0.258	253	14.7	1.9	43.1
	0.017	11	739	7	440	65.4	28.9	14.9	0.91	15.81	5.642	1.372	0.035	0.514	263	20.6	35.1	39.1
	0.01	18	1028	7.01	612	95.4	33.1	23.4	1.73	25.13	7.484	1.748	0.084	1.432	321	22.1	12.1	38.0
	0.0075	19	1053	6.89	627	105.8	33.3	28.32	2.21	30.53	8.02	1.927	0.115	-1.96	345	20.9	30.1	37.4
	0.01	14.5	1067	6.77	635	111.9	37.4	26.9	2.38	29.28	8.661	1.814	0.129	-2.48	341	26.1	29.1	29.3
	0.0131	12.5	873	7.5	519	85.7	29.4	20.5	1.89	22.39	6.696	1.768	0.069	1.036	289	15.2	5.5	41.3
	0.017	11.5	685	7.34	408	58.2	21.1	15.4	1.67	17.07	4.641	1.673	0.013	0.141	238	16.9	8.2	42.4
	0.016	12.5	719	7.22	428	68.6	24.4	17.5	0.58	18.08	5.431	1.705	0.019	0.233	246	19.2	3.1	29.4
	0.0094	17.5	1006	7.1	599	89.3	32.5	28.9	1.52	30.42	7.13	1.666	0.094	1.562	338	2.8	7.7	27.9
	0.009	19.5	1040	7.7	619	103.4	35.2	31.8	1.89	33.69	8.056	1.781	0.116	2.091	351	3.89	8.9	39.2
	0.008	20.5	1089	6.89	648	113.9	36.1	33.89	2.09	35.98	8.654	1.913	0.145	2.685	377	8.3	21.5	36.4
	Minimum	0.0075	11	685	6.77	408	58.2	21.1	11.2	0.58	11.93	4.64	1.37	-0.145	2.685	238	2.8	1.3
Maximum	0.018	20.5	1162	7.7	692	121.4	38.8	33.9	2.45	35.98	9	2.1	0.013	0.141	377	26.1	35.1	43.1
Average	0.0116	15.5	952.7	7.09	567.1	91.14	31.3	22.9	1.66	24.6	7.12	1.76	0.084	1.465	312	16.44	14.7	34.1
Σx	0.0037	3.29	163	0.26	97.1	20.28	5.366	7.1	0.58	7.37	1.43	0.16	0.045	0.91	44.9	6.87	11.8	8.16
Cv	0.317	0.21	0.171	0.036	0.171	0.223	0.172	0.31	0.351	0.3	0.201	0.09	-0.54	-0.62	0.144	0.418	0.801	0.24
Cv%	31.7	21.3	17.1	3.6	17.1	22.3	17.2	31	35.1	30	20.1	9	-54	-62	14.4	41.8	80.1	24

Table 4. Physical and chemical analyses and statistical parameters of the Al-Kura District wells water.

Well Name	Q m ³ /s	T °C	EC us/cm	pH Unit	TDS mg/l	Ca ²⁺ mg/l	Mg ²⁺ mg/l	Na mg/l	K mg/l	Na+K Mg/l	rCa ²⁺ +rMg ²⁺ meq/l	rCa ²⁺ /rMg ²⁺	SI _c	SI _d	HCO ₃ ⁻ mg/l	NO ₃ ⁻ mg/l	SO ₄ ²⁻ mg/l	Cl ⁻ mg/l
Bait Idis Well	0.042	17	769	7.7	458	90	28.7	17	2	19	6.852	1.902	-0.066	-0.968	382	16	17	33
	0.041	18	820	7.8	488	90	29.2	17	1.6	18.6	6.893	1.87	-0.063	-0.937	382	17	16.5	28
	0.043	17.5	827	7.9	492	90	27.5	17	1.6	18.6	6.754	1.984	0.072	-1.018	382	16.4	16	29
	0.062	15.5	783	7.4	466	83	28.2	25	3	28	6.461	1.785	0.063	-0.906	352	34	18	42
Judyta Well 1	0.058	16.5	798	7.28	475	85	28.4	27	0.1	27.1	6.578	1.814	0.065	-0.949	359	21.8	0	45
	0.044	16.5	781	7.26	465	90	28.8	27	0.1	27.1	6.861	1.895	-0.08	-1.175	359	21.1	0	40
	0.053	16	816	7.4	486	87	28.1	25	3.3	28.3	6.653	1.877	-0.07	-1.005	352	34	18.8	42
	0.056	16	785	7.24	467	88	29.3	22	3	28	6.802	1.821	0.072	-1.076	362	31	16	39
Judyta Well 2	0.082	14.5	719	7.14	428	79	28	27	0.1	27.1	6.246	1.711	0.054	-0.776	345	32.7	0	42
	0.047	16.5	729	7.47	434	90	29	28	1.1	29.1	6.877	1.882	0.073	-1.089	380	23	12	41
	0.065	15	764	7.18	455	82	27.5	27	0.1	27.1	6.354	1.808	0.059	-0.832	349	32.7	0	44
	0.058	17	785	7.24	467	88	28.1	22	2.6	24.6	6.703	1.899	0.079	-1.136	362	31.3	17	39
Tabaqat Fabel-1	0.028	17.5	959	7.59	571	102	30	47	4	51	7.559	2.061	0.097	-1.499	410	15	35	66
	0.027	17.5	984	7.7	586	103	31.1	47	4	51	7.698	2.008	0.097	-1.549	417	14	37	70
Tabaqat Fabel-3	0.057	15	954	7.44	568	86	27.8	44	4.6	48.6	6.578	1.876	0.066	-0.94	355	28.3	53	81
	0.063	15.5	966	7.46	575	82	27.9	44	4.6	48.6	6.387	1.782	0.059	-0.844	351	28.8	53.8	88
	0.025	18.5	984	7.75	586	103	29.1	47	3.9	50.9	7.533	2.146	0.101	-1.504	417	13.7	37	70
Tabaqat Fabel-5	0.024	18	944	7.76	562	103	30	41	3	44	7.608	2.081	0.089	-1.364	413	16.5	33	64
Tabaqat Fabel-6	0.039	17.5	897	7.7	534	98	30.2	37	3	40	7.375	1.968	0.096	-1.485	406	17	30	56
Tabaqat Fabel-9	0.029	18	973	7.35	579	102	31	44	4	48	7.641	1.995	0.094	-1.491	420	16	37	70
Minimum	0.024	14.5	719	7.14	428	79	27.5	17	0.1	18.6	6.25	1.711	0.101	-1.549	345	13.7	0	28
Maximum	0.082	18.5	984	7.9	586	103	31.1	47	4.6	51	7.7	2.146	0.054	-0.776	420	34	53.8	88
Average	0.0472	16.66	851.85	7.5	507.1	91.1	28.9	31.6	2.49	34.24	6.9	1.91	0.076	-1.127	377.8	23.02	22.4	51.45
Σx	0.0158	1.16	93.73	0.233	55.83	7.9	1.1	11	1.56	11.98	0.48	0.112	0.015	0.26	26.82	7.67	16.56	17.68
Cv	0.3349	0.07	0.11	0.031	0.11	0.09	0.04	0.35	0.63	0.35	0.07	0.06	0.197	-0.23	0.071	0.333	0.74	0.344
Cv%	33.49	6.97	11	3.105	11	8.7	3.78	34.81	62.7	35	6.85	5.86	19.74	-23	7.1	33.32	74.1	34.37

Table 5. Comparison of the coefficients for chemical and physical variations of Al-Dhaher Cave Spring with Ain Zubia, Ain Zgaeg, and Al-Kura wells.

Variable	Al-Dhaher Cave Spring	Ain Zubia	Ain Zgaeg	Al-Kura wells	min	max	average	σx	Cv%
Chemical Variables									
Ca ²⁺ (mg/l)	69.56	93.293	91.14	91.05	69.56	93.293	86.26	11.2	13
Mg ²⁺ (mg/l)	27.3	22.533	31.287	28.895	22.533	31.287	27.51	3.7	13.4
Na ⁺ (mg/l)	16.86	1.657	22.899	31.6	1.657	31.6	18.25	12.6	69
K ⁺ (mg/l)	0.706	1.323	23.636	2.485	0.706	23.636	7.04	11.1	158
rCa ²⁺ +rMg ²⁺ (meq/l)	5.717	6.51	7.122	6.921	5.717	7.122	6.57	0.62	9.5
rCa ²⁺ /rMg ²⁺	1.535	2.486	1.755	1.908	1.535	2.486	1.92	0.41	22
SI _c	-0.053	-0.105	-0.084	-0.076	-0.105	-0.053	-0.1	0.02	-27
SI _d	-0.758	-1.28	-1.465	-1.1271	-1.465	-0.758	-1.16	0.3	-26
HCO ₃ ⁻ (mg/l)	285	322.2	311.867	377.75	285	377.75	324.2	38.99	12
NO ₃ ⁻ (mg/l)	25.3	16.6193	16.439	23.015	16.439	25.3	20.34	4.5	22
SO ₄ ²⁻ (mg/l)	12.12	12.1733	14.73	22.355	12.173	22.355	15.35	4.83	32
Cl ⁻ (mg/l)	25.58	26.82	34.08	51.45	25.58	51.45	34.48	11.92	35
Physical Variables									
Q (m ³ /s)	0.0008	0.0098	0.012	0.0472	0.0008	0.047	0.02	0.02	118
T (°C)	14.3	14.57	15.47	16.675	14.3	16.675	15.25	1.07	7
EC (us/cm)	805.4	976.3	952.7	851.85	805.4	976.33	896.56	81.28	9
TDS (mg/l)	479.4	581.2	567.0	507.1	479.4	581.2	533.69	48.39	9
pH (unit)	7.216	6.9747	7.1	7.488	6.975	7.488	7.19	0.22	3

Table 6. Coefficients of variations of Al-Dhaher Cave Spring, Ain Zubia, Ain Zgaeg, and Al-Kura wells comparison with Rock Spring (Jacobson and Langmuir, 1974), Iskrets Spring (Eftimi and Benderev, 2007), and Thomson Spring (Jacobson and Langmuir, 1974).

Variable	Al-Dhaher Cave Spring	Ain Zubia	Ain Zgaeg	Al Kura wells	Rock Spring Conduit type	Iskrets Spring Conduit type	Thomson Spring Diffusive type
Chemical Variables							
Ca ²⁺	18.1	23.0	22.3	8.7	25.5	11.7	6.4
Mg ²⁺	8.4	12.7	17.2	3.8	27.6	30.0	2.0
rCa ²⁺ +rMg ²⁺	14.3	19.6	20.1	6.9	-	6.34	-
rCa ²⁺ /rMg ²⁺	9.9	13.8	9.0	5.9	-	28.2	-
SI _c	40	47.1	54.0	19.7	18.7	35.5	16.1
SI _d	47.7	56.2	62.0	23.0	-	28.8	-
HCO ₃ ⁻	6.8	23.2	14.4	7.1	28.6	14.2	2.7
NO ₃ ⁻	27.8	57.9	41.8	33.3	32.0	46.7	19.9
SO ₄ ²⁻	26.2	101	80.1	74.1	12.7	43.7	17.8
Cl ⁻	40.8	32.7	24	34.4	17.7	24.5	29
Physical Variables							
Q (m ³ /s)	43.4	28.4	31.7	33.5	175	94.2	26.3
T (°C)	14.5	20.1	21.3	7.0	26.9	10.3	1.4
pH (unit)	2.3	1.4	3.6	3.1	1.7	1.6	0.6

Conclusions

The results of geochemical study and water analyses clearly showed that the aquifer system is prone to karstification and clearly showed the impact of karst body on the chemical composition of the spring waters.

The significant variations of the Al-Dhaher Cave Spring flow rate were found to influence the alteration of main ions concentrations that characterize groundwater-rock interaction. The results also showed that the input water is aggressive to the rock component, but the output water is generally over saturated in respect to rock components. The flow rate variations also lead to a change of karstification activity indicators.

As a result there is a strong relationship prevailing between the quality and physical and chemical characteristics of spring's water in the study area, with the karstification processes that lead to the formation of limestone caves, and still those physical and chemical processes have an impact strong and accelerated the dissolved of carbonate rocks and composition caves karst. In addition, to helping water rainfall from the Earth's surface to the bottom, as well as the impact of rising and percolating groundwater act to top.

Further, it was found that Al-Dhaher Cave Spring is of conduit type as water moves mainly in large fractures, joints and solution openings. The spring is recharged by the infiltration of the

precipitation in the Al-Dhaher Cave Spring karst basin and via sinkholes. Also, this study reveals that the main controlling factor of the chemistry of Al-Dhaher Cave Spring is the lithology of rocks, seasons and time to discharge of the spring.

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