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Hydro-Geochemistry and Application of Water Quality Index (WQI) for Ground Water Quality Assessment, Wadi Al-Samen—Hebron—West Bank

Waseem Al-Tamimi[1]*, Fadoua Hamzaoui-Azaza[2], Marwan Ghanem[3], Rachida Bouhalila[1]

[1]Modeling Hydraulic and Environmental Laboratory, National Engineering School of Tunis, University of Tunis El Manar, Tunis, Tunisia
[2]Laboratory of Sedimentary Basins and Petroleum Geology (SBPG), Geology Department, Faculty of Sciences of Tunis, University of Tunis El Manar, Tunis, Tunisia
[3]Department of Geography, Birzeit University, Ramallah, West Bank, Palestine
Email: *waseem.altamimi@enit.utm.tn

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Abstract

Located south of the West Bank, Wadi Al-Samen is considered one of the most important sources of groundwater recharge for the eastern aquifer in Hebron. It is polluted by sewage originating from domestic and industrial consumption in the Hebron area. Water quality assessment is an important criterion for achieving sustainable development. To evaluate water quality, twenty samples were collected from groundwater sources for two seasons and were analyzed for Physical properties (Total dissolved solids (TDS), Electrical conductivity (EC), potential hydrogen (pH), Temperature (T)), Four major cations (Mg^{2+}, Ca^{2+}, Na^+ and K^+), and the Major anions (HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-); geochemical methods such as Piper scheme were used for the sample result analysis. To characterize wastewater components, six samples were collected from the Wadi discharge for two seasons and were analyzed (potential hydrogen (pH), Electrical Conductivity (EC), Total Dissolved Solid (TDS), Total Suspended Solids (TDS), Total Suspended Solids (TSS), Biological Oxygen Demand (BOD_5), and Chemical Oxygen Demand (COD). The results of nitrate levels showed that 20% of the ground water samples exceeded the standard limit of the World Health Organization (WHO). The quality of drinking water was assessed using the Water Quality Index (WQI), which suggests that 10% of samples are classified from poor to very poor. The abundance of cations from highest to lowest was found to be: Ca; Mg; Na, and for the anions it is HCO_3; Cl; SO_4. The dominant hydrochemical facies of 35% of collected aquifer samples reveal that Ca-Mg-Na-Cl-HCO_3 are in the domain. Evaluation of irrigation suitability was performed using parameters of Sodium adsorption ratio (SAR), electric conductivity (EC), and Salinity. The results in both rounds for EC showed that all water sources are suitable for irrigation according to Todd's classification. SAR was not suitable in three water resources samples. Wilcox analysis for the two seasons revealed that 85% of samples are not appropriate for irrigation uses.

Keywords

Drinking and Irrigation Suitability, Water Quality, WHO Guidelines, Wadi Al-Samen, West Bank

1. Introduction

Water quality is affected by the quantity and quality of supplies coming from various sources [1] Geochemical exploration of groundwater is one of the most important methods used to identify patterns of mineralization [2]. The process of infiltrating groundwater to depth increases the chances of mineralization compared to surface geochemical methods [3]. Hydrochemical information closely contributes to developing an understanding of groundwater systems and tracing historical developments [4].

The process of geochemical exploration of groundwater lies in understanding the interactions between water and rocks, and the mechanism of transferring elements in the secondary environment [5]. The possibility of groundwater penetration into the depths of the earth's crust increases the chances of discovering mineralization and Water rock interaction processes [3].

Attention to geochemistry has become an urgent necessity due to the increase in human projects that pollute the environment, such as underground liquid waste storage, the spread of sanitary landfills, the artificial feeding of aquifers, and accidental water pollution [6]. The risk of groundwater pollution increases with the continuous increase in the population, and urban and agricultural development, due to the increasing dependence of people in their daily life on groundwater sources for agricultural, industrial and irrigation uses [7] [8].

Water interacts with rocks to varying degrees because of environmental and weather changes; mineral development in groundwater is concentrated on water rocks that contain carbonate minerals, while silicate minerals do not interact easily with rocks [9]. To find out the health risks associated with groundwater consumption, geochemical processes are studied to determine hydrogeochemical properties, understand geochemical processes, study groundwater chemistry and its important health role, and assess its risks to human health as a result of the interaction of water with rocks and other materials [10]. Groundwater is affected by many important factors that make up the hydrochemical footprint of groundwater. These factors are not limited to interactions between rocks and water and the effect of geological layers on determining the concentration of groundwater. These factors include rainfall chemistry, groundwater survival time, vegetation cover, soil processes chemistry Mineralogy and Pollution [11].

The study of geochemical processes helps in determining the flow of water, knowing the sources of groundwater, and improving predictions of the origin of pollutants and their means of transport and paths in the groundwater systems [12]. The process of moving groundwater between geological layers below the subsurface from one region to another faces a large number of chemical processes, and a change occurs in its chemical composition in colour, taste and smell. These processes include interaction with gases in the unsaturated zone and the chemical composition of recharge water in addition to water interactions with some human activities [13]. The investigation of the quality of groundwater chemistry is one of the hot topics and raises international interest due to its close association with sustainable development and environmental policies [14].

To understand groundwater patterns and verify the integrity of 20 water samples in the Wadi Al-Samen basin, collected from aquifers for two seasons and were analyzed for Physical properties (Total dissolved solids (TDS), Electrical conductivity (EC), potential hydrogen (pH), Temperature (T)), Four major cations (Mg^{2+}, Ca^{2+}, Na^{+} and K^{+}),and the Major anions (HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-); and interpreted using statistical and geochemical methods.

The main objectives of this research are to study the hydrochemistry of groundwater and its interactions, determine the proportions of basic minerals in it, and the purposes of using water in Wadi Al-Samen for human and agricultural consumption, using collection methods through geographic or geochemical information systems.

2. Study Area

Site Description

Wadi Al-Samen area is located in Hebron city in the southern area of the West Bank (**Figure 1**), 36 km south of Jerusalem city. The total area of the Hebron governorate is 1036 km^2; these areas compose 16% of the West Bank, in which elevation ranges from 100 m above sea level to 1021 m.

In the Hebron area, many stone and marble industries dispose of wastewater within the sewage network. This leads to an increase in the percentage of sawdust that reaches the wastewater network towards the valley, Where untreated sewage flows from the wastewater network along Wadi Al-Samen, south of Hebron [15].

The environmental damage resulting from untreated sewage in Wadi Al-Samen is a serious issue [16]. Factories such as tanneries, slaughterhouses, metallurgical, electronic and dairy transfer the untreated wastewater into the sewer system in Hebron city. Towns and villages in the Hebron Governorate lack a sewage network due to the common cesspits, septic tanks and open drains for sewer disposal which may flood into untended lands in Wadi Al-Samen.

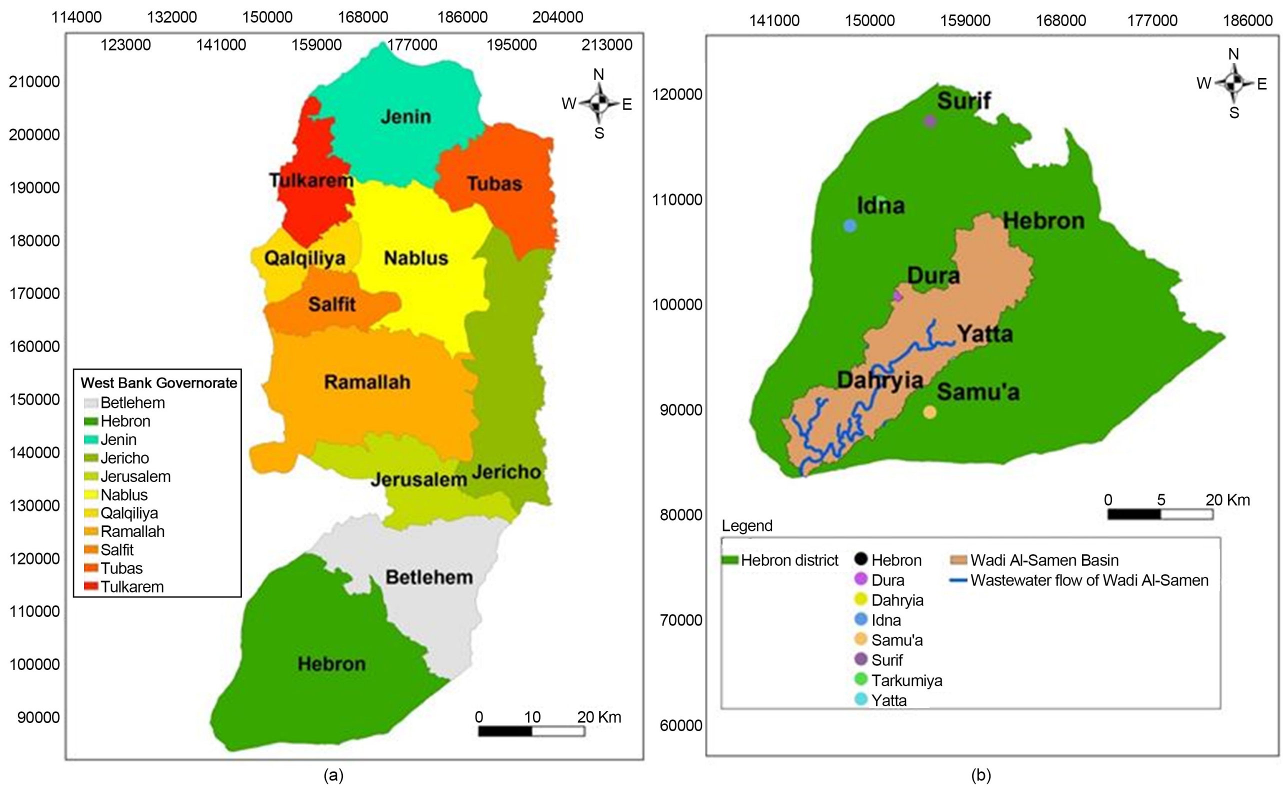


Figure 1. Location of the study area (a) the West Bank (b) Hebron District, Wadi Al-Samen Basin.

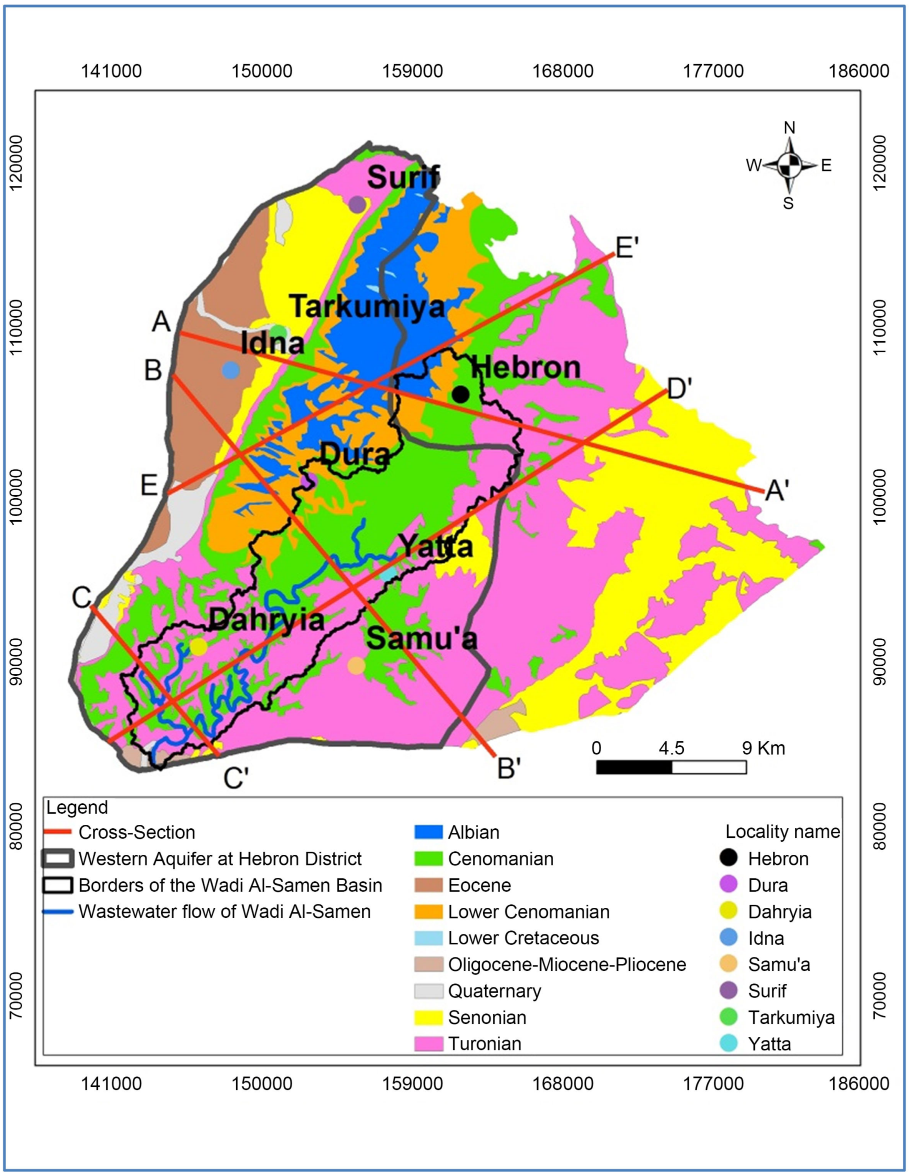
These conditions allowed the infiltration of wastewater which contaminates both the shallow and deeper aquifers including Al Fawwar wells which are highly contaminated with nitrates exceeding the international and national Parameters [17].

There is no effective wastewater system for industrial or household purposes in Hebron city [18]. Wadi Al-Samen starts from an altitude of 759 meters above sea level and extends until it reaches a height of 400 meters above sea level [19]. The climate in Hebron city is affected by the Mediterranean Sea [20].

3. Geology and Hydrogeology

The geological formation in the West Bank consists of a deep fault line in the earth's crust. There are two parallel series of mountains by the fault line near the West Bank where the mountains are divided into three parts: the Nablus Mountains, the Jerusalem Mountains and the Hebron Mountains (Jabal al-Khalil) and the Jordan Valley is surrounded by mountains [21].

The area lacks geological studies and there are various difficulties in identifying different geological features and understanding tectonic phenomena as well as drawing the structural framework of the aquifer system. However, this geological study was based on the classification of stratigraphic features and the determination of geological structures and characteristics of Wadi Al-Samen as shown in (**Figure 2**). Stratigraphy and lithology of the Wadi Al-Samen Catchment showed that it contains sedimentary carbonate rocks from Albanians to Eocene age, according to [22] the study area in Hebron.



141000
150000
159000
168000
177000
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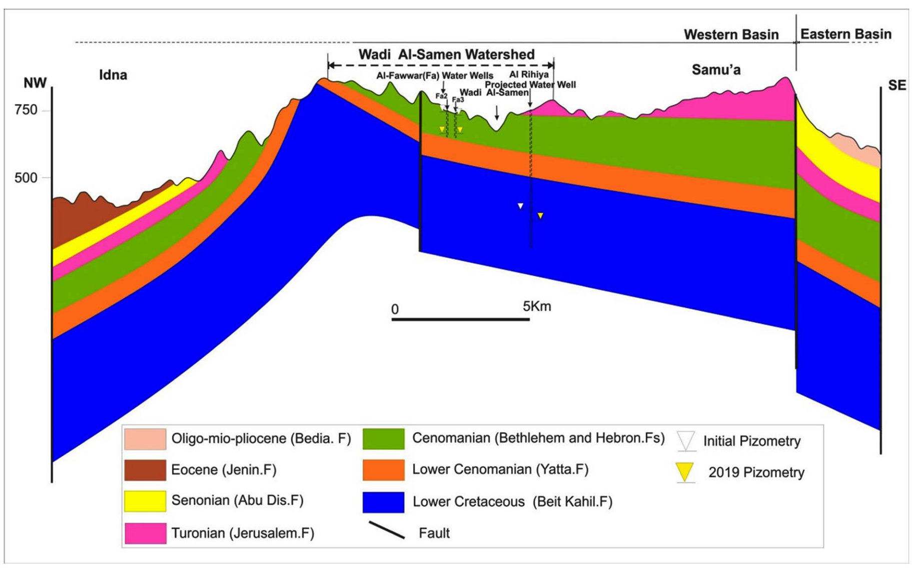
W
E
S
Surif
Tarkumiya
Idna
Hebron
Dura
Yatta
Dahryia
Samu'a
A
A'
B
B'
C
C'
D'
E
E'
0
4.5
9 Km
Legend
Cross-Section
Western Aquifer at Hebron District
Borders of the Wadi Al-Samen Basin
Wastewater flow of Wadi Al-Samen
Albian
Cenomanian
Eocene
Lower Cenomanian
Lower Cretaceous
Oligocene-Miocene-Pliocene
Quaternary
Senonian
Turonian
Locality name
Hebron
Dura
Dahryia
Idna
Samu'a
Surif
Tarkumiya
Yatta



Western Basin
Eastern Basin
Wadi Al-Samen Watershed
Al-Fawwar(Fa) Water Wells
Al Rihiya Projected Water Well
Wadi Al-Samen
NW
SE
Idna
Samu'a
750
500
0
5Km
Oligo-mio-pliocene (Bedia. F)
Eocene (Jenin.F)
Senonian (Abu Dis.F)
Turonian (Jerusalem.F)
Cenomanian (Bethlehem and Hebron.Fs)
Lower Cenomanian (Yatta.F)
Lower Cretaceous (Beit Kahil.F)
Fault
Initial Pizometry
2019 Pizometry

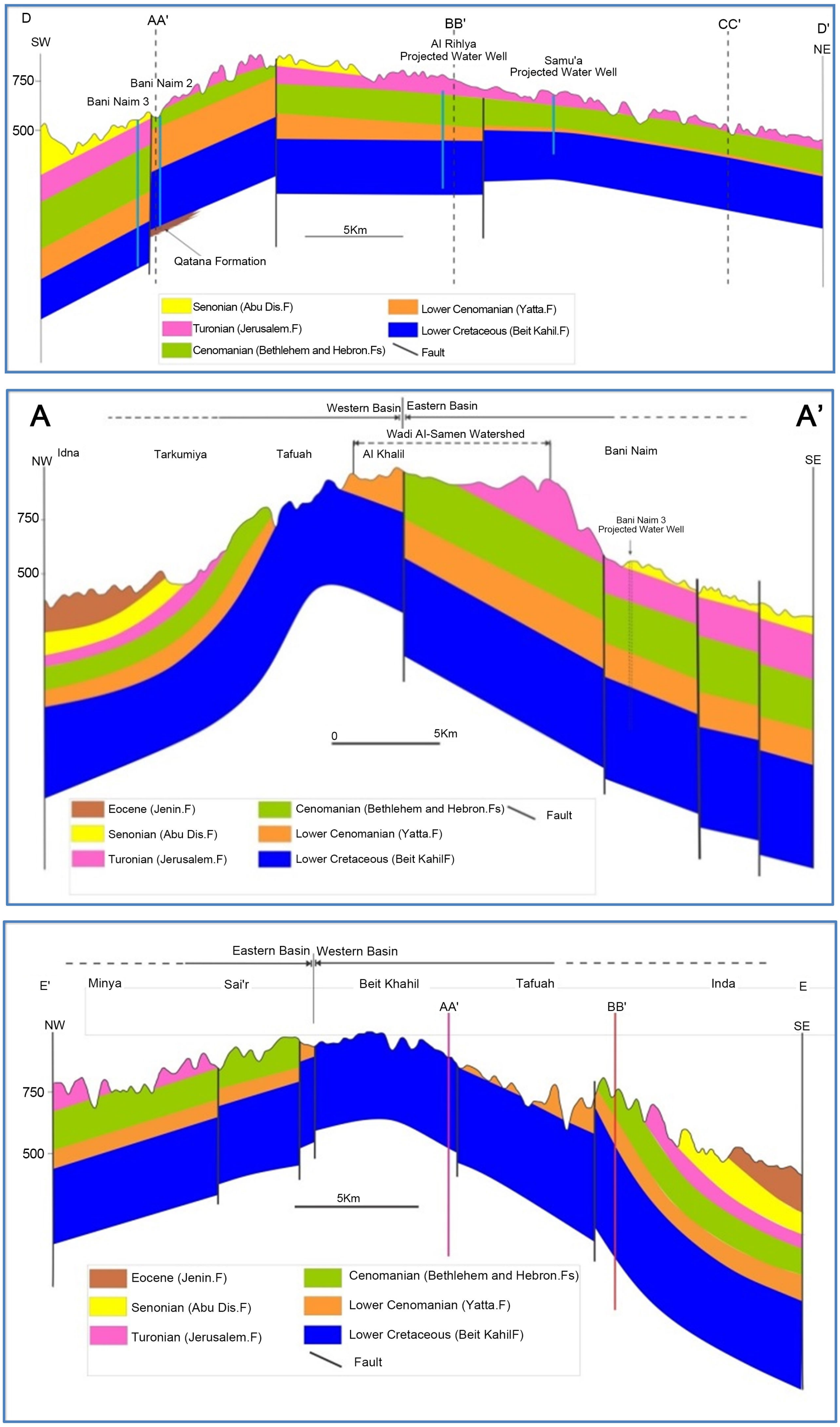


Figure 2. Geological strata and cross-section of Hebron Governorate and the boundaries of Wadi Al-Samen Basin.

The lower aquifer thickness reaches 300 m and consists of limestone and dolomite, the lower layer of the aquifer is divided into two configurations, one of which is the Upper Beit Kahil Formation and the other the lower Beit Kahil Formation and the formation layer is not completely separate because the water flows through fractures, cracks and joints. The Upper Beit Kahil Formation is Karstic and consists of marl and limestone but the lower Beit Kahil Formation consist of dolomite and limestone the upper aquifer layers are separated from the lower aquifers by the formation of Yatta, which is composed of marl and clays with some chalk and has a thickness of 50 - 150 m [23].

The upper layers of the southern West Bank consist of Limestone, dolomite, and chalky Limestone with Different geological formations of the regions and their elevations.

This study heavily relied on data obtained from drilling the main wells; this is due to the scarcity of information and gaps of knowledge in this field and place. These include Al-Samu'a, Al-Rihiya, AL-Fawwar 1, Al-Fawwar 2, Bani naim 2, and Bani naim 3 which are located in some of the borders of the region of study, to prepare illustrative geological sections for wells scattered in the study area as shown in (**Figure 3**) and (**Figure 4**).

The aquifers on the West bank are classified into three basins; Western, Eastern, and Northeastern and they all have been identified to be deep. Wadi Al-Samen watershed is located above an area of access that feeds into the Western basin and a small area on the head in the Eastern basin as shown in (**Figure 2**); this is of great importance and gravity because the discharge of wastewater over this area leads to pollution of groundwater quality in the Western basin [24].

4. Abstraction and Piezometry

There are no organized wells in the region, except for a few wells that were drilled during the period under the rule of the Kingdom of Jordan (such as Al-Fawwar, Rihiya and Al-Samu') before 1967 which were also rehabilitated by the local authorities. The only aquifer well that reaches the deep aquifers (**Figure 5**) is the Rihia well, with an extraction of 45 m^3/day. Water flows quickly through fractures, cracks and rock joints, which appear because of dissolution, Groundwater is stored in the upper layers of these cracks called karst, forming channels and expanding the fractures by dissolution [25].

The exploitation of both aquifers decreased the piezometric levels with the piezometry of the upper wells (Al-Fawwar 1, Al-Fawwar 3) decreasing in 2013 to 657 m at the beginning of drilled 715 m. Additionally, the Samu'a well decreased in 2016 to 434 m in comparison to 552 m at the beginning of drilled. The piezometry to the lower well (Rihiya), at the beginning of drilled 335 m, remained at the same level with slight fluctuation.

In this research, we look forward to achieving the main purposes related to study the hydrochemistry of groundwater, determine the impact of groundwater

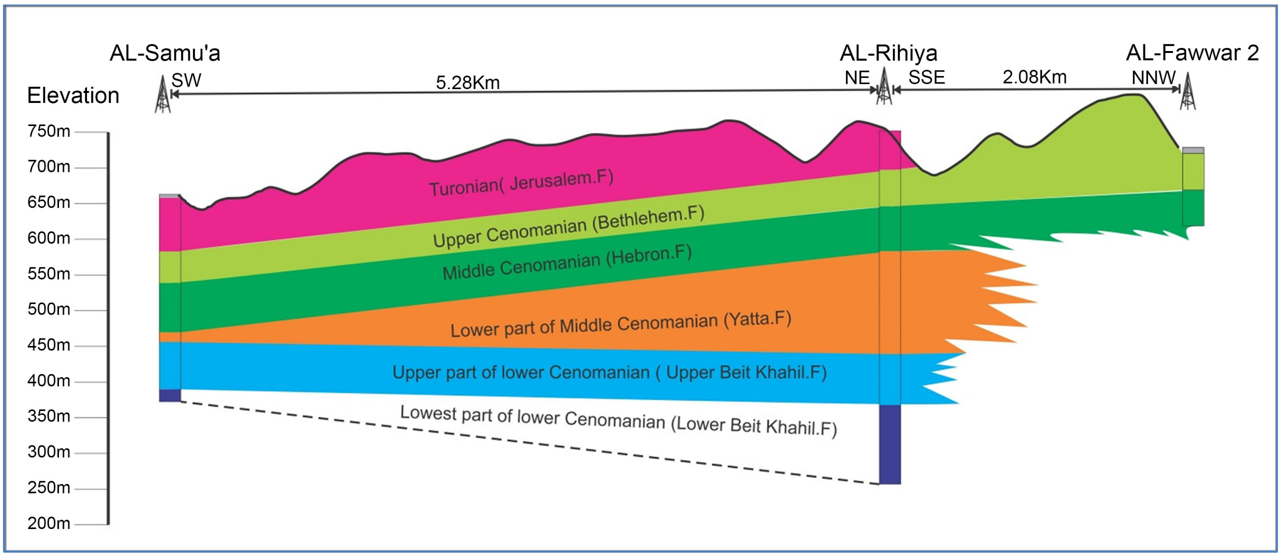


Figure 3. Correlation between Al-Samu'a, Al-Rihiya, AL-Fawwar 2 Wells.

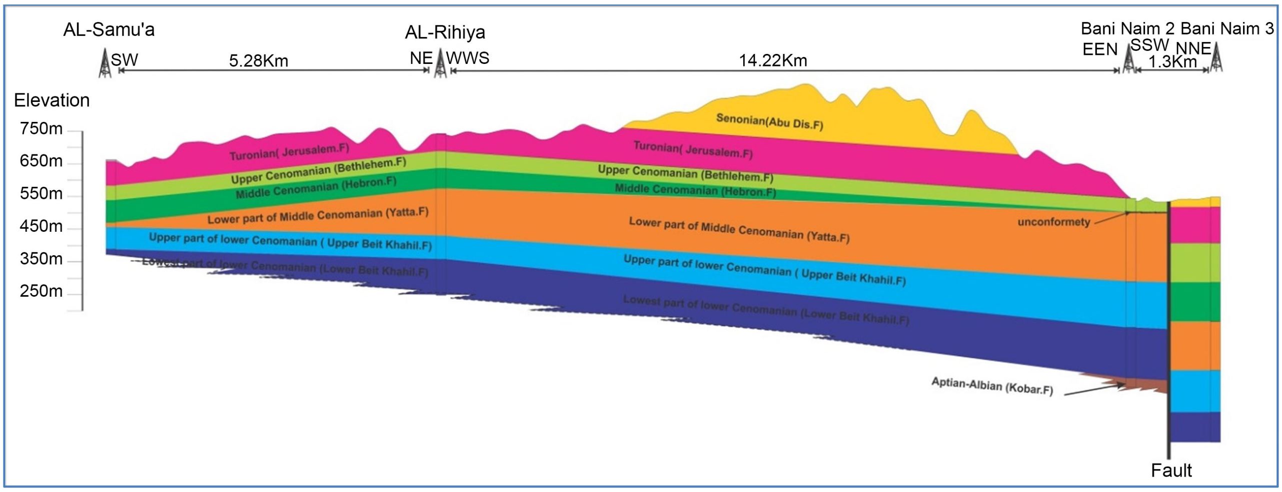


Figure 4. Correlation between Al-Samu'a, Al-Rihiya, Bani Naim 2, Bani Naim 3 Wells.

pollution with wastewater, to determine the quality of groundwater in wells, and to identify wells where groundwater is suitable or unsuitable for drinking, irrigation purposes and to determine the characterization of wastewater.

5. Materials and Methods

The methodological approach used in this study is shown in (**Figure 6**) as a flow chart.

6. Samples Collection and Analysis

6.1. Wastewater Samples

Two rounds consisting of 12 composed of 8 consecutive 3 hours cycle wastewater samples—six samples each round—were collected along the Wadi stream (**Figure 7**). Samples were collected, preserved and prepared according to standard method of wastewater [25]. Samples were analyzed for pH, EC, BOD_5, COD, TSS, and TDS.

6.2. Ground Water Samples

20 groundwater resources (wells and springs) were collected in September 2019 and May 2020 which corresponded to dry and wet seasons (**Figure 8**). The groundwater samples were collected (in duplicate) in pre-washed polypropylene sampling bottles (1000 L plastic bottles for chemical tests). Groundwater was collected after pumping the wells for about 10 min and rinsing the bottles twice with the water to be sampled. Water was filtered through 0.45 μm millipore membrane filters to separate suspended particles.

The Electrical conductivity (EC μS/cm), total dissolved solids (TDS), pH and Temperature were measured on site, using portable conductivity and pH meters, after recalibration with standard buffer solutions. These variables were measured using portable field instruments.

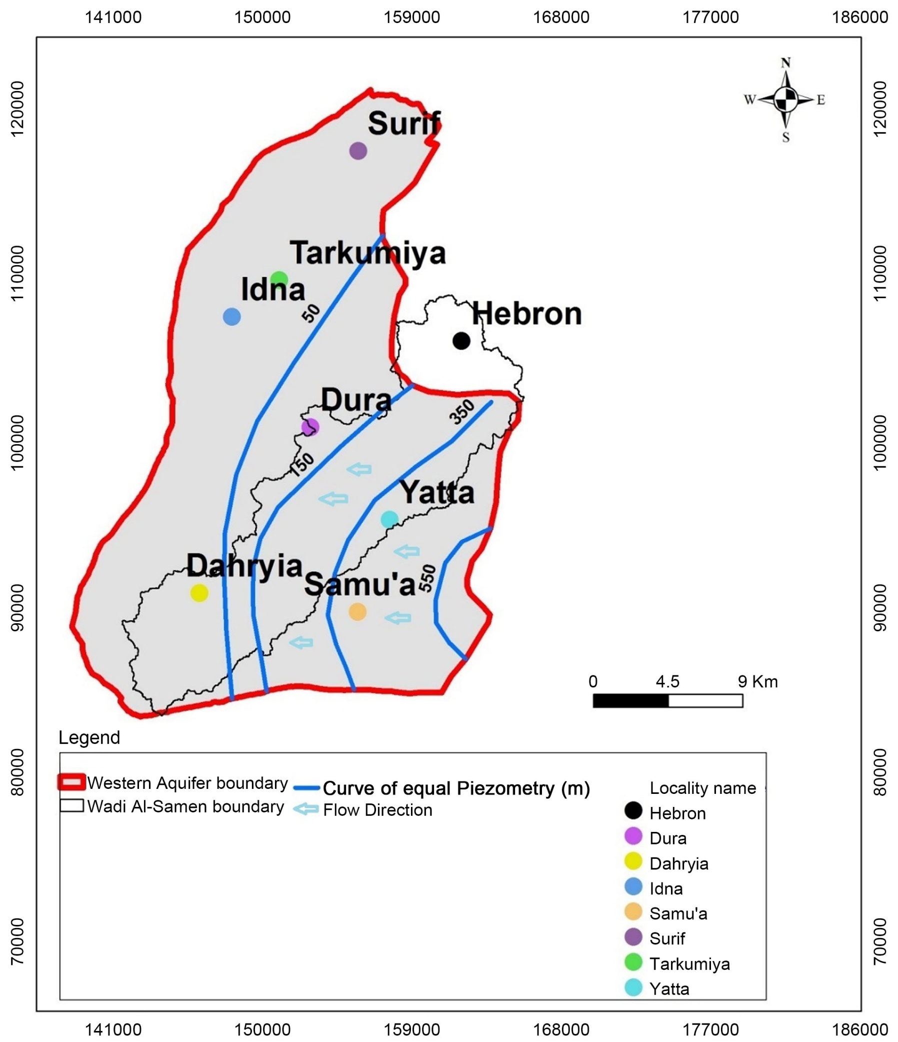


Figure 5. Piezometric maps.

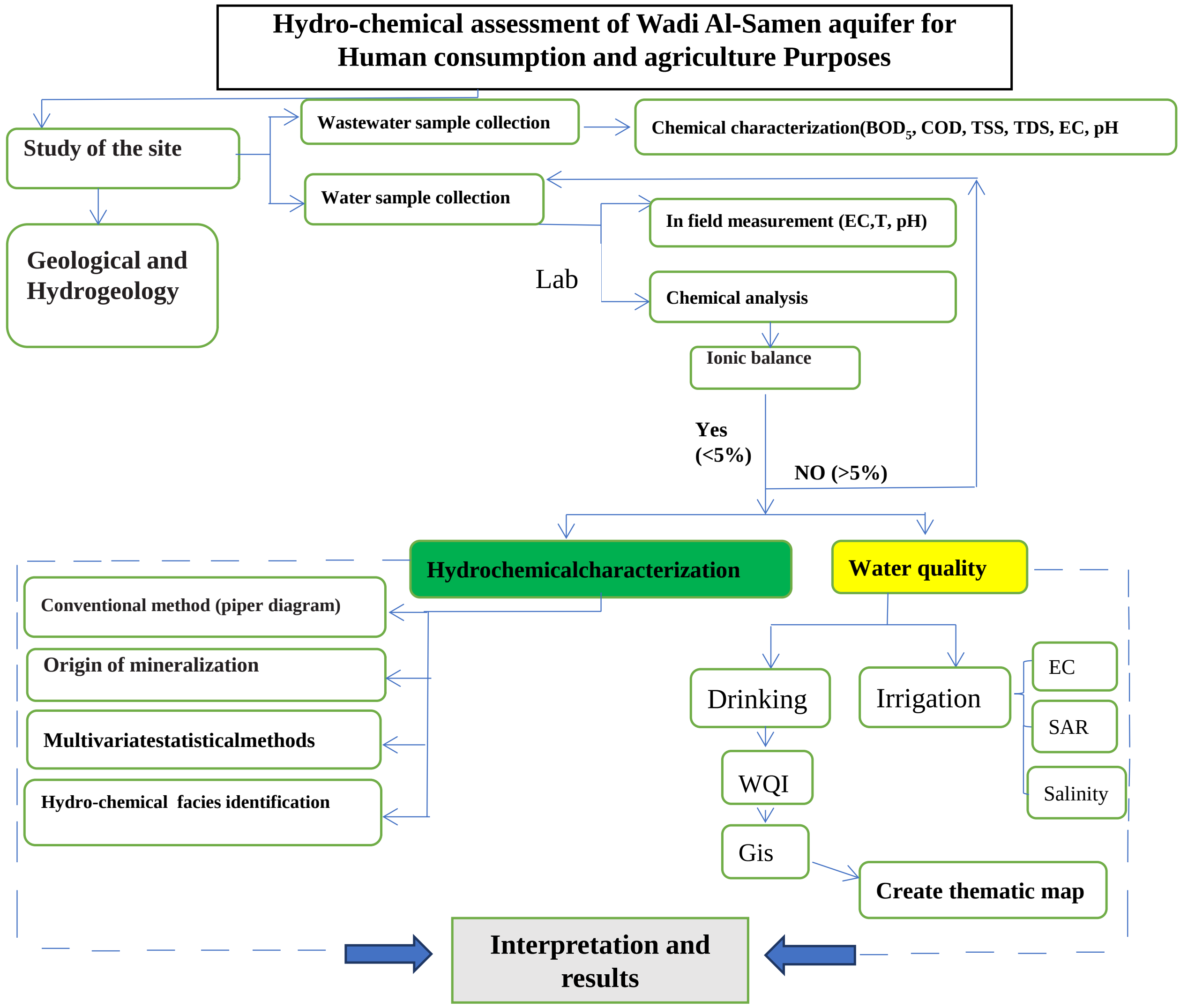


Figure 6. Flowchart illustrating the methodology applied for evaluation of groundwater of Wadi Al-Samen.

The samples were analyzed for the following major cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}); and anions (Cl^-, SO_4^{2-}, HCO_3^-, and NO_3^-). Water samples meant for cation analyses were acidified with HNO_3^- to decrease the pH. Samples taken from the field were labeled and taken to the laboratory and stored at temperatures below 4˚C and the analytical work was completed within 7 days from the date of sampling. Major cations were analysed by atomic absorption spectrometer, after calibration of the instrument with known standards.

Major anions (SO_4^{2-}, Cl^- and NO_3^-) were analyzed by ion chromatograph. Concentration of HCO_3^- in groundwater was determined by acid titration method, as prescribed by the American Public Health Association [26].

To verify the results of analysis for all samples, the charge balance errors (%E) was calculated by the following Equation (1) [27] [28].

$$\%E = \frac{\Sigma C - \Sigma A}{\Sigma C + \Sigma A} \quad (1)$$

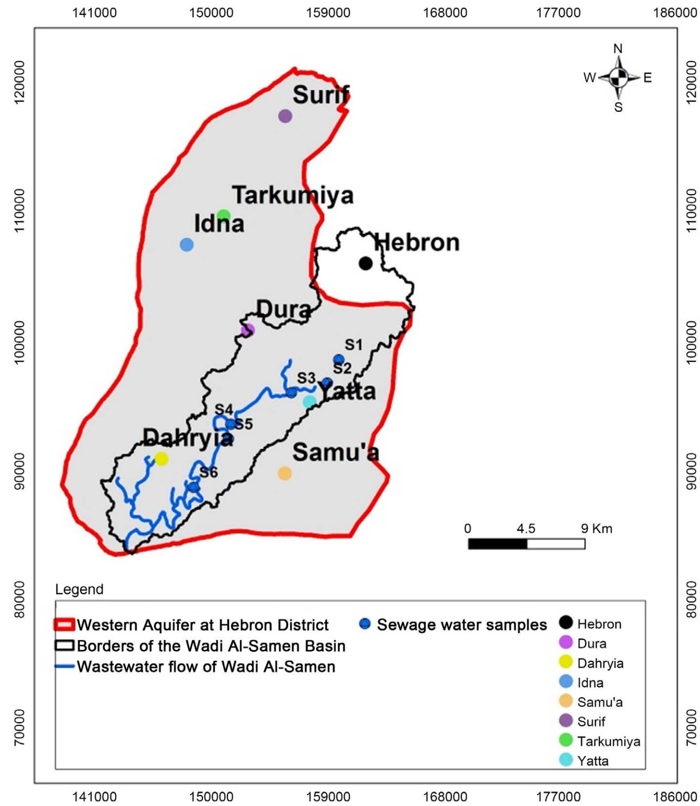


Figure 7. Wastewater samples in Wadi Al-Samen Basin.

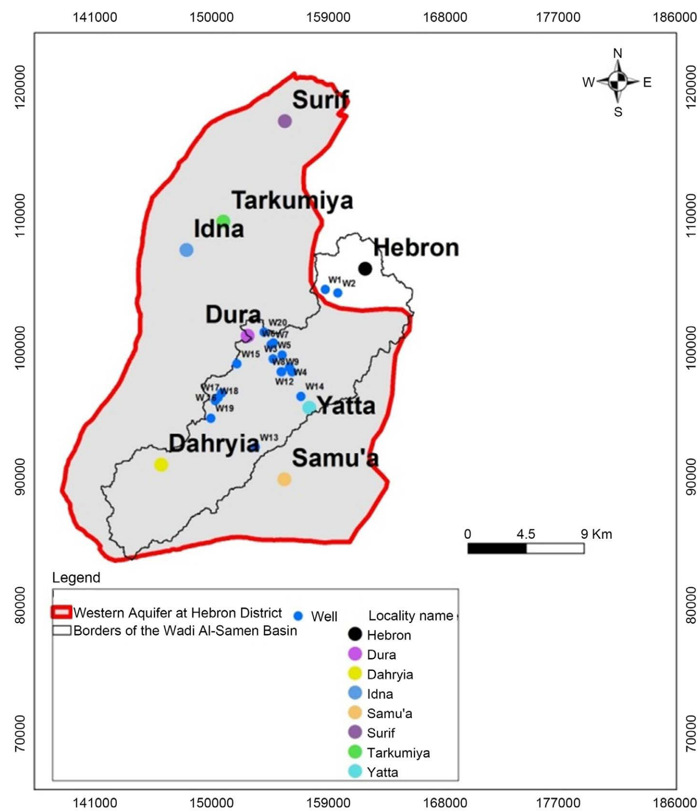


Figure 8. Ground water samples in Wadi Al-Samen Basin.

where $\%E$ is the charge balance errors, C is cations in meq/l, A is anions in meq/l. Examination of the charge balance to Wadi al Samen samples are judged perfectly (average $\%E \approx 2.05\% < 5\%$).

7. Hydro-Chemical Characterization

7.1. Conventional Methods

The determination of the hydrochemical processes of the aquifer of Wadi AL-Samen was obtained through the creation of the Piper scheme [29].

7.2. Multivariate Statistical Methods

Multivariate statistical methods are applied to monitoring data sets. The most common analysis method is hierarchical cluster analysis (HCA) [30] [31].

The hierarchical classification tree represents dry season samples, for the wet season. The physicochemical parameters were analyzed in 20 samples collected in 2019-2020 for two seasons; these variables (pH, T, TDS, EC, Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, HCO_3^-, and SO_4^{2-}) were successfully used in hierarchical cluster analysis (HCA).

7.3. Evaluation of Irrigation Suitability

To evaluate the irrigation water quality in wadi Al-Samen basin were used three ionic parameters in (mg/l) such as (EC-Todd (2007), SAR (alkalinity hazard) (Equation (2)), Salinity (Wilcox diagram):

$$\mathrm{SAR} = \frac{\mathrm{Na}}{\sqrt{\frac{\mathrm{Ca} + \mathrm{Mg}}{2}}} \tag{2}$$

7.4. GIS Analysis

GIS database has been developed to obtain data for better understanding to Wadi Al-Samen Basin. Under ArcGis 10.3, the database for the study site was created and all wells were identified, Identify its main characteristics and historical data such as (pumps, piezometer). IDW method was used to created water quality indicators (WQI) to spatial distribution maps.

8. Results and Discussion

The steps of this research are summarized according to the scheme in (**Figure 6**)

8.1. Wastewater

8.1.1. pH

pH results were ranged between 6.4 - 8.1. It changes along the flow of the stream due to the change in the characterization of the wastewater. It was noted that there is a heavy load of industrial wastewater at the end of the sewage network in Hebron, which is the first point of discharge to the stream of Wadi Al-Samen. The main component of that wastewater is clay from stone cut industrial discharge.

8.1.2. Electrical Conductivity (EC)

EC readings were slightly higher due to dry season as results of two facts: dilution of ionized solutes by rainwater in wet season and evaporation effect in dry season with values ranging from 1462 - 3100 (μs/cm), they were within expected ranges of raw wastewater in Palestinian community. However, high values of EC were found in El-Hellh (S2) and Wadi Al Door (S1) as a result of the rainfall loads. These are the first 2 sampling points of wastewater stream (**Figure 7**). Wastewater flow affects its quality because the longer the flow the less pollutants concentrations will be. On other hand, and as a direct effect of hot summer, the evaporation helped to concentrate pollutants by reducing solvent volume and accordingly EC values were higher during dry season.

8.1.3. Total Dissolved Solid

Total Dissolved Solids (TDS), which is defined as the measurement of dissolved materials in water, such as inorganic salts and organic matter, it is critical to assess TDS for wastewater treatment purposes.

TDS maximum value obtained for from Wadi Al-Samen samples was (2000 mg/l) in dry season and (1500 mg/l) in wet season due to the dilution of wastewater. The maximum value of Total Dissolved Solids obtained from samples of Wadi Al-Samen in wet season was (1500 mg/l); this is due to the dilution of wastewater by precipitation. Less than it in the dry season was as follows (2000 mg/l).

8.1.4. Total Suspended Solids

Total Suspended Solids (TSS), is defined as any type of solid materials that is insoluble in wastewater but that can be captured by a filter; this includes both industrial and domestic wastes. In the case of Wadi Al-Samen, samples from El-Hellh (S2) and Wadi Al Door (S1) had high concentrations in both seasons as a direct result of discharge from stone cut industry, where TSS had lower concentrations in the other 3 samples, as the heavy clay loads settled down along the stream. On other hand, autumn samples' tests were higher from the spring ones because of the evaporation effects as well as the longer working days in summer time so the industrial wastewater discharge is higher and more concentrated.

8.1.5. Biological Oxygen Demand

As abbreviated (BOD_5), it represents the amount of organic present in water pollution, and it is a measure of water pollution with organic materials. The concentration of dissolved oxygen in the water is monitored, as a result of the consumption of oxygen levels by organic materials. BOD results were elevated near El-Hellh (S2) & Wadi Al Door (S1) as direct results of industrial wastewater discharge directly into stream. It was also higher in autumn samples than winter, and this is due to the dilution of wastewater by precipitation. BOD_5 ranged between 241 to 918 mg/l in dry season and 213 to 698 mg/l in wet season.

8.1.6. Chemical Oxygen Demand (COD)

The main sources of increased COD content are industrial, agricultural and animal activities. COD values are usually 50% - 60% higher than BOD_5 values. Low values of COD content were found in Wadi Al Dahriya (S6) samples as they are far from the exit of the sewage pipes and therefore yield lower values of COD.

8.2. Ground Water Hydrochemistry

8.2.1. Physical Properties

1) **TDS**: the majority of samples collected from groundwater resources gave TDS values between 300 - 900 mg/l. Samples taken from Al-Alaqa Al-Foqa (W19) and Al-Baiarah (W4) ranged between 1000 - 1200 mg/l, indicating sewage infiltration into groundwater aquifers. The high values in TDS are due to the geochemical processes that are represented by rainwater infiltration, evaporation, ion exchange, and anthropogenic sources such as agricultural activities, domestic sewage [32].

2) **EC**: Electric Conductivity values for samples collected from springs ranged from 500 - 2000 μS/cm, and 500 - 1000 μS/cm for samples collected from the ground wells. In summer, results were of higher values in ground wells mainly in Al-Rihia (W14) and Al-Fawwar wells (W11, W12) and reached to 500 - 1100 μS/cm. These high results of EC are attributed to the wells Al-Rihia and Al-Fawwar in the summer, due to their proximity to human activities, which are mainly agricultural lands, causing increases in ionic concentration.

3) **pH**: The water of Wadi Al-Samen has a neutral or slightly basic pH, the pH value of samples ranged from 7.39 - 7.8, These pH values are typical for the area [33], these values fall within the accepted standard range 6.5 - 8.5 according to WHO.

4) **Temperature**: In the dry season, slightly higher temperatures were recorded compared to the wet season, which explains their storage at surface levels. Most of the samples collected from groundwater resources gave values of temperature ranged 20.5 - 21.5 degrees Celsius.

8.2.2. Water Chemistry

1) **Major cations:**

Four major cations (Mg^{2+}, Ca^{2+}, Na^+ and K^+) were analyzed. The results showed high values Ca^{2+} which exceeds WHO accepted range that is 200 mg/l [34]. These elevated values of Ca^{2+} could be explained by the direct effect of active stone industry in the area where wastewater discharges directly to the nature. The levels of K^+ were also high in some samples because of the non-regulated use of fertilizers. Mg^{2+} and Na^+ were within accepted limits and considered as natural presence elements.

The prevalent cation tendency in Wadi Al-Samen aquifer is $Ca^{2+} > Na^+ > Mg^{2+} > K^+$.

Calcium is the common cation in Wadi Al-Samen aquifer for two seasons, its concentration for dry season ranges between 39.79 and 251.9 mg/l with an average of 116.45 mg/l. Table 1 and its concentration for wet season ranges 34.5 to 240.8 with an average 106.36 mg/l Table 2. Sodium is the second most common predominant cation has a concentration for dry season ranging from 24.93 to 182.2 mg/l with an average of 65.72 mg/l and for wet season ranges from 18.3 to 176 mg/l with an average 58.65 The high sodium values are due to cation exchange between minerals, human activities and poor drainage conditions. Groundwater samples did not exceed the threshold of the WHO and the maximum allowable level is 200 mg/l.

In general, the concentrations of sodium and calcium ions are generally higher compared to those of magnesium ions. The dry season values range from 10.72 to 87.01 mg/l with an average value of 41.13 mg/l and for wet season 10.69 to 84 with an average of 37.50 mg/l. Additionally, potassium quantities in dry season range from 1.563 to 19.81 mg/l with an average of 7.76 mg/l; and for the wet season ranging from1.561 to 19.808 with an average of 7.5.

2) Major anions

The most abundant anions are (HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-). By measuring the concentrations of these ions in groundwater samples, the composition of the anions (side by side with cations) is determined for water; the chemical quality of the water type can be determined and described. A brief summary of anions concentrations in dry and wet seasons is presented in Table 1 & Table 2. Cl^- analysis for most of springs were higher than the allowed range (250 mg/l) as some springs are saline springs that follow from shallower aquifers or at the land surface. NO_3^- also increased in (Al Fawwar 1, 2) (W11, W12), Khursa (W16) and Abdo (W17) (accepted limit 50 mg/l), this because of wastewater stream and manmade pollution with excess quantities of fertilizers. Show anions concentrations during 2 seasons. (Figure 9), (Figure 10) Nitrates and salinity are the most frequently polluted groundwater [35].

9. Statistical Study of the Water Resources of Wadi Al-Samen Basin

Hierarchical cluster analysis

The analyzed water samples are represented by a hierarchical classification tree Figure 11; Figure 12 confirms the results obtained by the piper chart. There are different combinations:

For dry season:

Cluster 1: consists of the most mineralized wells with highly Na^+, HCO_3^-, Ca^{2+}, Cl^-.

Cluster 2: consists of the most wells composed of the least mineralized with the enrichment of SO_4^{2-}.

For wet season:

Cluster 1: consists of the most mineralized wells with highly Na^+, HCO_3^-, Ca^{2+}, Cl^-.

Cluster 2: consists of the least mineralized wells with a slight enrichment in mg^+.

Table 1. Summary of statistical calculations of chemical types for dry season from Wadi Al-Samen wells.

	pH	EC	T	TDS	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{2-}
Min	7.23	385	19	213	5	39.79	10.72	24.93	1.563	59.8	100.5	6
Max	8.02	2330	24	1278	546.9	251.9	87.01	182.2	19.81	190.6	789.4	23.1
Stand. dev	0.2469	456.7	1.3945	259.5	120.06	57.76	17.12	41.5	5.7	26.7	177.95	4.2
mean	7.696	1115.1	21.6	636.6	53.36	116.45	41.13	65.72	7.76	143.9	287.6	16.1
Std. error	0.0552	102.1	0.31	58.028	26.846	12.915	3.825	9.2792	1.2799	5.967	39.791	0.94
Median	7.73	1014.5	21	612	13.5	109.05	38.905	55.135	7.6395	141.6	259.8	16.05
Variance	0.06097	2086	1.94	67343.8	14414.06	3335.88	292.67	1722.1	32.77	711.9	31665.7	17.76

Table 2. Summary of statistical calculations of chemical types for wet Season from Wadi Al-Samen wells.

	pH	EC	T	TDS	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{2-}
Min	7.3	380	18	240	5	34.5	10.69	18.3	1.561	58.3	87	5
Max	7.9	2298	23	1304	546.9	240.8	84	176	19.808	186.9	754	22.9
Stand. dev	0.1928	478.845	1.538	263.307	120.429	56.723	16.946	40.748	5.284	23.15	174.83	3.781
mean	7.67	1055.6	20.45	641.3	51.76	106.36	37.50	58.65	7.5	134.5	277.13	15.51
Std. error	0.04	107.07	0.3439	58.878	26.929	12.684	3.7892	9.1116	1.1816	5.178	39.1	0.85
Median	7.7	967	20.5	601	11	95.44	35.45	46.4	7.635	133	253.6	15.8
Variance	0.037	229293.8	2.366	69330.7	14503.7	3217.5	287.16	1660.4	27.921	536.1	30564.5	14.3

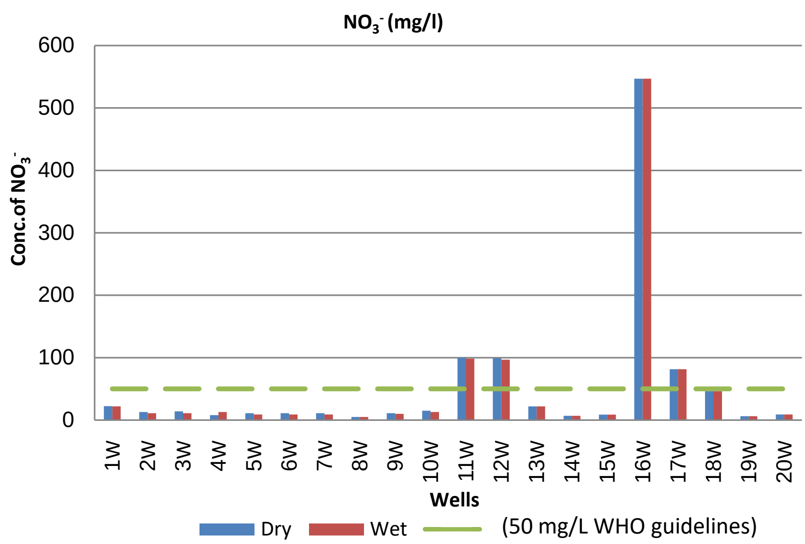


Figure 9. NO_3^- concentrations for all samples in two rounds.

10. Geochemical Facies

Water Type

The Piper scheme was used to classify water samples as an effective representation of chemical elements and by using a program Aquachem program through Piper's scheme, Figure 13. It showed samples from springs and wells in the two seasons (dry and wet) located in earth alkaline with predominant bicarbonate.

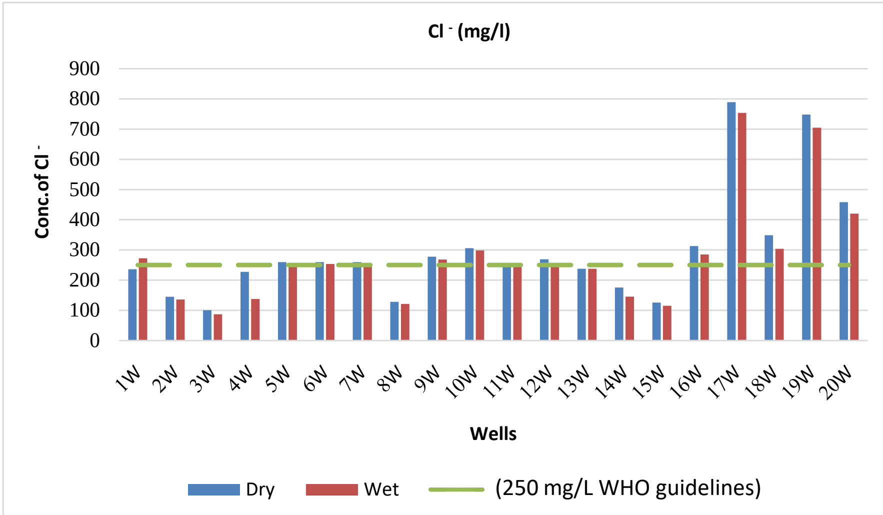


Figure 10. Cl^- concentrations for all samples in two rounds.

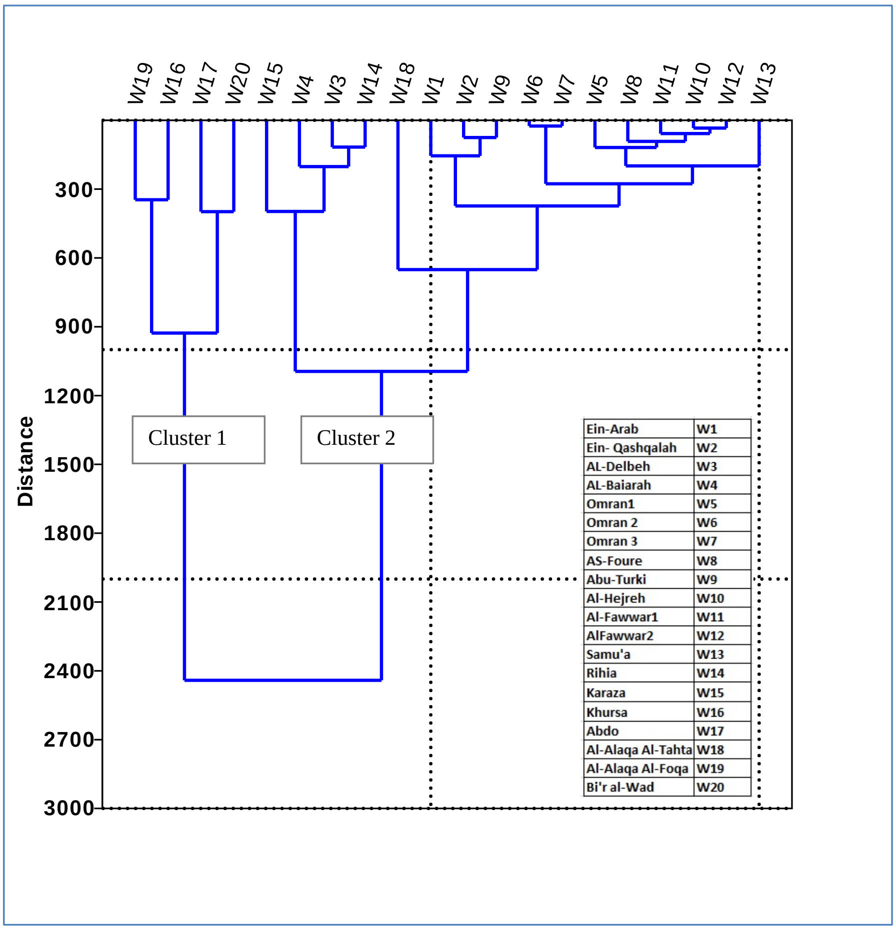


Figure 11. Hierarchical water classification tree for Wadi AL-Samen aquifer in dry season (Ward's method, Euclidean classification).

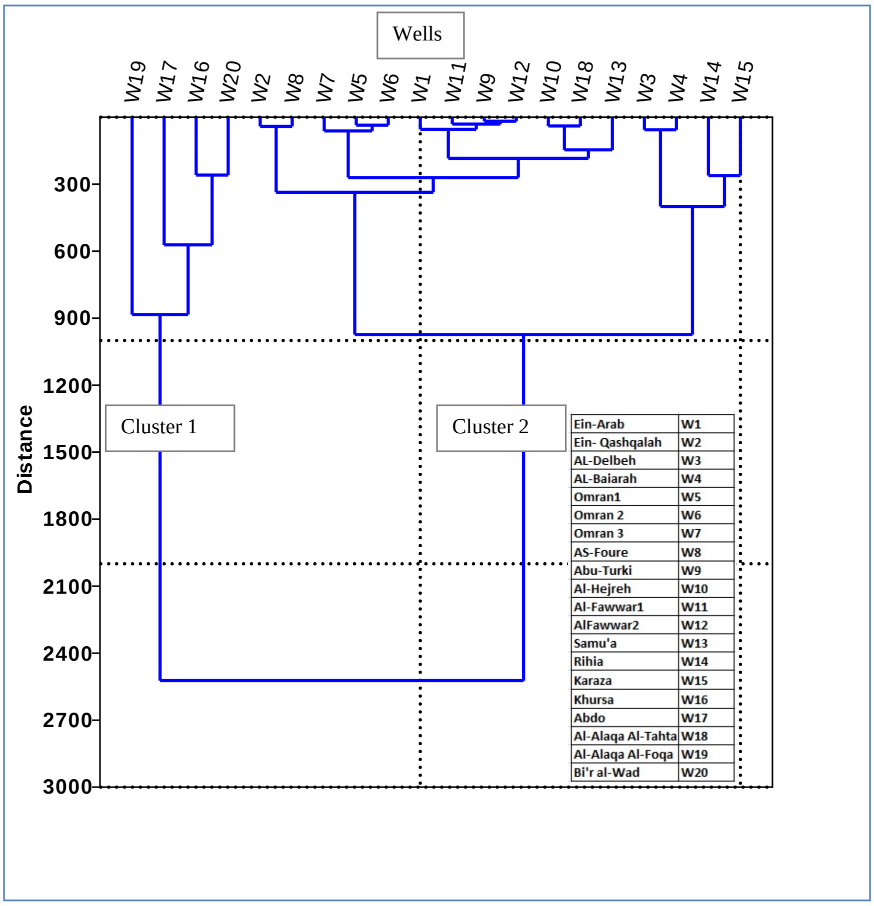


Figure 12. Hierarchical water classification tree for Wadi Al-Samen aquifer in wet season (Ward's method, Euclidean classification).

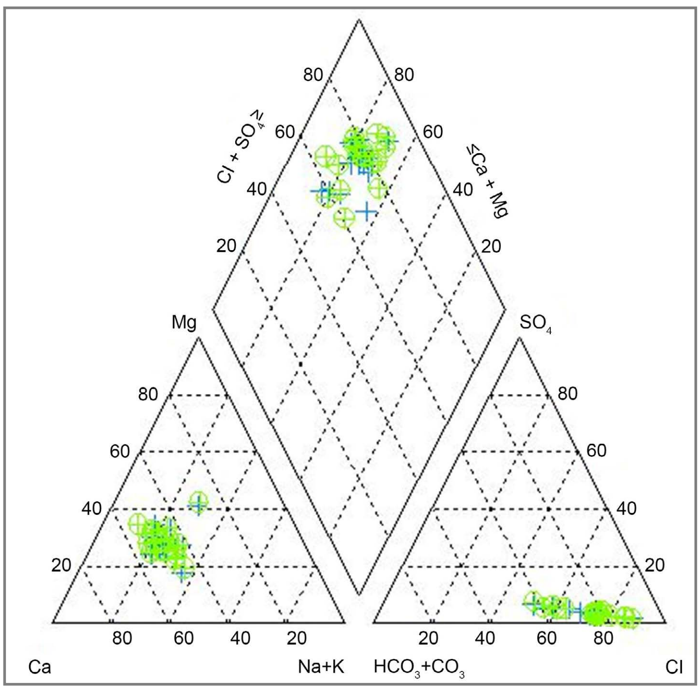


Figure 13. Piper diagram for two seasons of Wadi Al-Samen Basin.

The results showed that the determination of water type Table 3 depends on nature and is the indicator of the interaction of limestone rocks; it appeared that 35% of samples are located in domain of Ca-Mg-Na-Cl-HCO_3. 20% of the samples showed that water type of Ca-Mg-Cl-HCO_3, 15% of the samples showed that water type of Ca-Na-Mg-Cl and 30% from samples water type of Ca-Mg-Na-Cl, Ca-Mg-Cl.

11. Water Quality Index (WQI)

Estimation and mapping of water quality index

Water quality is evaluated in any given area by using physical, chemical and biological tests [36] [37]. The study focuses on parameters that are considered harmful to human health and the environment if they exceed specific values. Human consumption is described using one of the most effective indicators to describe water quality by means of the Water Quality Index; The Water Quality Index is widely used in Europe, Africa and Asian countries [38] [39] [40].

Table 3. The water types for two seasons in Wadi Al-Samen Basin.

Dry Samples	Water type	Wet Samples	Water type
W1	Ca-Mg-Na-Cl-HCO_3	W1	Ca-Mg-Na-Cl-HCO_3
W2	Ca-Mg-Na-Cl-HCO_3	W2	Ca-Mg-Na-Cl-HCO_3
W3	Ca-Mg-Cl-HCO_3	W3	Ca-Mg-Cl-HCO_3
W4	Ca-Mg-Cl-HCO_3	W4	Ca-Mg-Cl-HCO_3
W5	Ca-Mg-Na-Cl	W5	Ca-Mg-Na-Cl-HCO_3
W6	Ca-Mg-Na-Cl	W6	Ca-Mg-Na-Cl-HCO_3
W7	Ca-Mg-Na-Cl	W7	Ca-Mg-Na-Cl-HCO_3
W8	Mg-Ca-Na-Cl-HCO_3	W8	Mg-Ca-Na-Cl-HCO_3
W9	Ca-Mg-Na-Cl-HCO_3	W9	Ca-Mg-Cl-HCO_3
W10	Ca-Mg-Na-Cl-HCO_3	W10	Ca-Mg-Na-Cl-HCO_3
W11	Ca-Mg-Cl	W11	Ca-Mg-Cl
W12	Ca-Mg-Cl	W12	Ca-Mg-Cl-HCO_3
W13	Ca-Mg-Na-Cl-HCO_3	W13	Ca-Mg-Na-Cl-HCO_3
W14	Ca-Mg-Cl-HCO_3	W14	Ca-Mg-Cl-HCO_3
W15	Ca-Na-Cl-HCO_3	W15	Ca-Na-Cl-HCO_3
W16	Ca-Na-Mg-NO3-Cl	W16	Ca-Mg-Na-NO_3-Cl
W17	Ca-Na-Mg-Cl	W17	Ca-Na-Mg-Cl
W18	Ca-Cl	W18	Ca-Na-Mg-Cl
W19	Ca-Na-Mg-Cl	W19	Ca-Na-Mg-Cl
W20	Ca-Na-Cl	W20	Ca-Na-Mg-Cl

The first step in evaluating of the water index begins by determining the necessary parameters as follows (pH, TDS, Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, Ca^{2+}), then the weight (w_i) is determined on the basis of (Mg^{2+}, Na^+ and K^+). In addition, to assess their expected effects on primary health, so that the parameters are assigned a maximum weight of 5. In the present study, the "weight" numbers given to the physico-chemical parameters are: 5 to NO_3^-, TDS, SO_4^{2-}; 4 to pH; 3 to Cl^-, Ca^{2+}, Na^+ and Mg^{2+}; 2 to K^+ and 1 to HCO_3^-.

Due to the importance of the main parameters in evaluating water quality sources (total dissolved solids, chloride, sulfates, and nitrates), and due to the minuscule role of bicarbonate Weight not less than one, and other parameters such as (calcium, magnesium, sodium and potassium), Depending on the importance of these parameters in evaluating the quality of drinking water, a weight is assigned that starts from 1 to 5.

The second step, the relative weight (W_i) of each parameter is computed using Equation (3):

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \tag{3}$$

where: w_i: is the weight of each parameter, n: is the number of parameters, W_i is the relative weight. The WHO standards for each parameter are given in Table 4.

During the third step, the quality evaluation scale (q_i) was calculated. For each parameter using Equation (4):

$$q_i = \frac{C_i}{S_i} \times 100 \tag{4}$$

where: q_i: is the quality rating, C_i: is the concentration of each chemical parameter in each water sample in milligrams per liter, S_i: is the WHO standard for each chemical parameter in mg/l.

Table 4. The weight and relative weight of each of the chemical parameters.

Parameters	WHO Standard	Weight (w_i)	Relative Weight (W_i)
pH	8.5	4	0.117647059
TDS	1000	5	0.147058824
NO_3^-	50	5	0.147058824
Ca^{2+}	200	3	0.088235294
Mg^{2+}	50	3	0.088235294
Na^+	200	3	0.088235294
K^+	30	2	0.058823529
HCO_3^-	280	1	0.029411765
Cl^-	250	3	0.088235294
SO_4^{2-}	250	5	0.147058824
Total		$\sum w_i = 34$	$\sum W_i = 1$

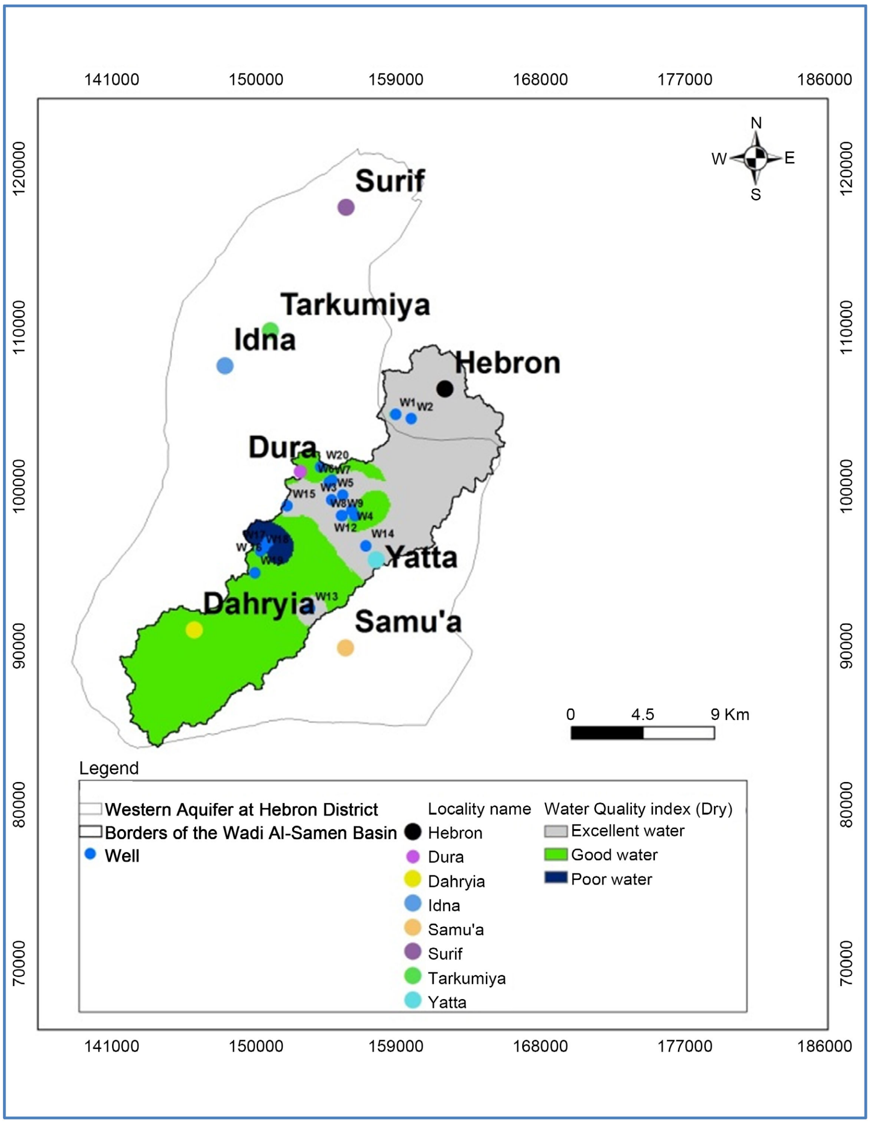
The fourth step involved is the calculation of the value of "Sub-Index" (SI_i) of ith parameter and computation of sum-total of sub-indices of all parameters (*i.e.*, Water Quality Index), For calculating the WQI, the SI_i is first determined for each chemical parameter using Equation (5), which is then used to determine the WQI as per the Equation (6):

$$SI_i = W_i \times q_i \quad (5)$$

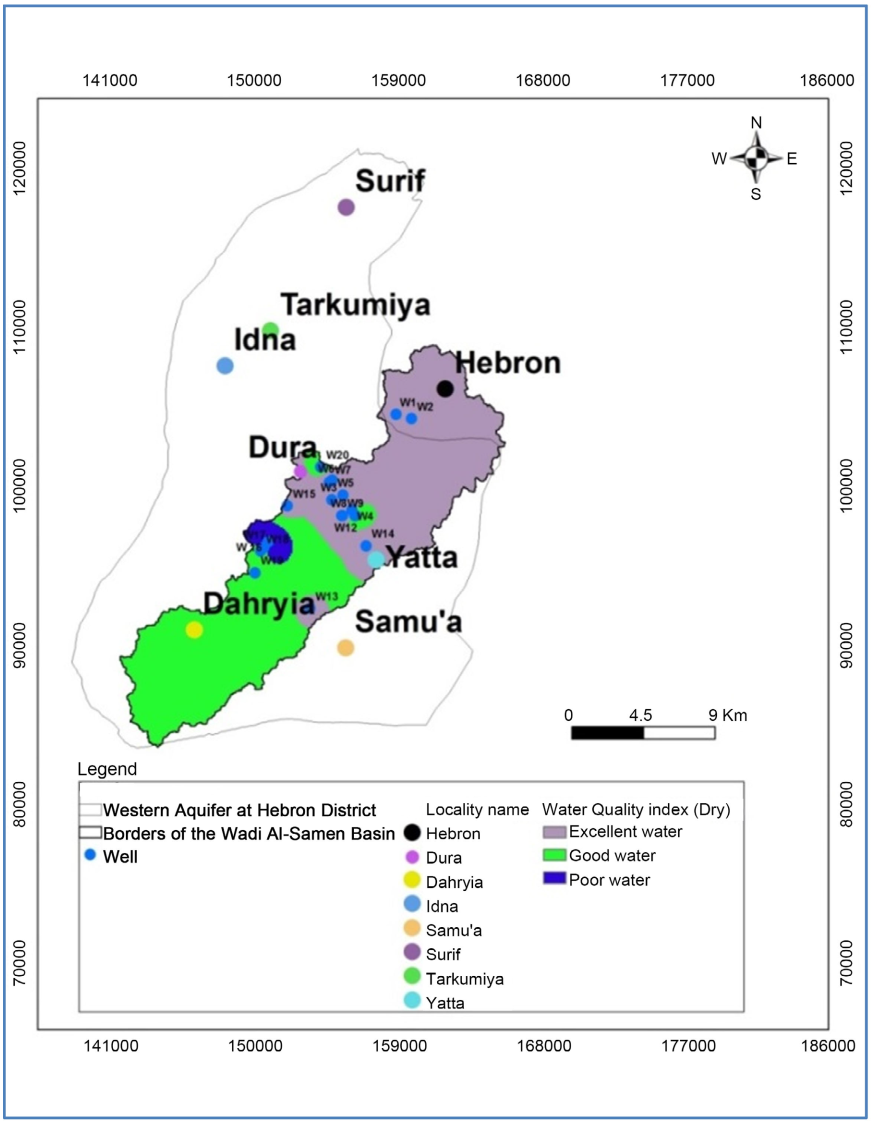
$$\text{WQI} = \Sigma SI_i \quad (6)$$

SI_i: is the sub-index of ith parameter, q_i: is the rating based on concentration of ith parameter, n: is the number of parameters.

The calculated WQI values are classified into five categories describing the water situation through Table 5: excellent, good, poor, very poor, and unfit for human consumption. The spatial distribution of water quality based on (WQI) as shown as in Figure 14(a), Figure 14(b).



(a)



(b)

Figure 14. The spatial distribution of water quality index for (a) dry season and (b) wet season.

Table 5. Water quality index (WQI) rating of groundwater samples [41] & [42].

WQI range	Type of water
<50	Excellent water
50 - 100.1	Good water
100 - 200.1	Poor water
200 - 300.1	Very poor water
>300	Unfit for drinking

12. Water Resources Suitability for Different Purposes

12.1. EC of Springs

Todd's classification was used to determine the ability of groundwater wells to irrigate crops, human consumption purposes. According to Todd's classification as shown in **Table 6**, the results in both rounds showed that all water sources are suitable for irrigating all kinds of crops.

12.2. Sodium Adsorption Ratio (SAR)

SAR is a predominant indicator to show the suitability of water quality for irrigation which based on the water content of Na^+, Ca^{2+} and Mg^{2+} by using Equation (2).

The results showed that in both seasons, the water from the tested springs are perfectly (Excellent) suitable for irrigation. This is because the SAR values are below 10, which means low salinity effects. However, water resources of Abdo (W17)13.90, Al-Alaqa Al-Foqa (W19)11.39 and Bi'r al-Wad (W20)10.24 were not found to have a good evaluation for Irrigation suitability based on SAR classifications of irrigation suitability **Table 7**.

12.3. Salinity

Wilcox diagram is a Semi-logarithmic diagram describing the relationship between sodium adsorption ratio (SAR) and electrical conductivity (EC). Scatter position (SAR) represent (risk of sodium) in the y axis and (EC) a represent (risk of salinity) in the x axis. As for the internal structure of the Wilcox diagram, it is divided into four columns (C1-C4) describing the salinity hazard, and four horizontal columns describing the sodium hazard (S1-S4).

The results of Wilcox diagram in the two seasons showed that few of samples its suitability for agriculture, these samples located in medium salinity (C2) and low sodium (S1). The rest of the study samples were described as unsuitable for cultivation [45], being in medium salinity (C2) and low sodium (S1) as shown in (**Figure 15**).

Table 6. Classification of Todd (2007) for the tolerance of different types of crops by using the conductivity value [43].

Crop division	Low salt tolerance crops EC (μS/cm)	Medium salt tolerance crops EC (μS/cm)	High salt tolerance crops. EC (μS/cm)
Fruit crops	0 - 3000 Limon, Strawberry, Peach spricot, Almond, Plum Orange, Apple, Pear	3000 - 4000 Cantaloupe, Olive, Figs, Pomegranate	**4000 - 10,000** **Date palm**
Vegetable crops	3000 - 4000 Green beans, Celery, Radish	4000 - 10,000 Cucumber, Peas, Onion carrot, Potatoes, Sweet corn, Lettuce, Cauliflower, Bell pepper, Cabbage, Broccoli, Tomato	**10,000 - 120,000** **Spinach, Garden beets**
Field crops	4000 - 6000 Field beans	6000 - 10,000 Sunflower, Corn (field), Rice, Wheat	**10,000 - 16,000** **Cotton, Sugar beet.**

Table 7. Classification of water for irrigation suitability based on SAR [44].

SAR value	Irrigation suitability
<10	Excellent
10 - 18	Good
18 - 26	Fair
>26	Poor

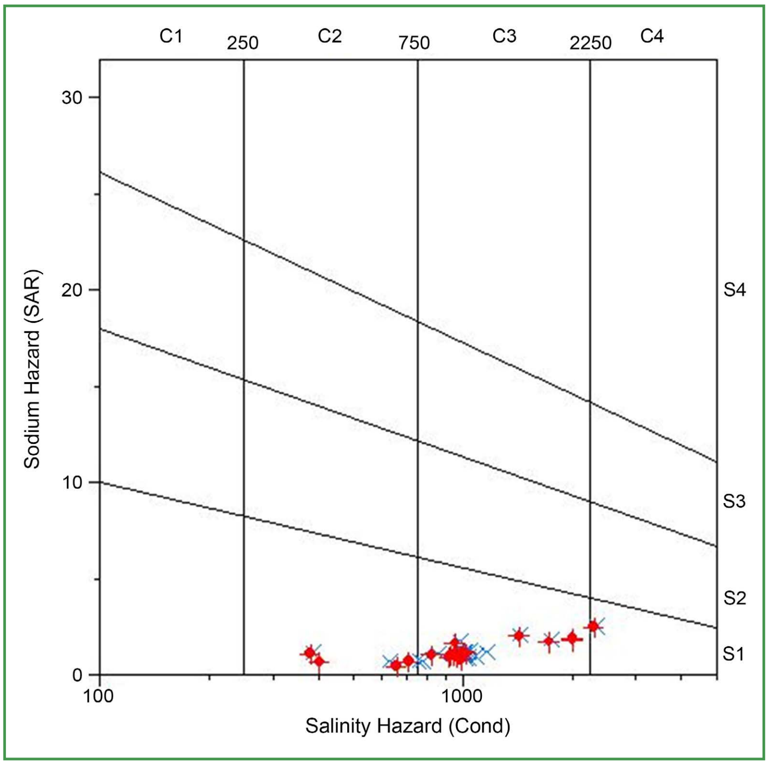


Figure 15. Wilcox classification of the water samples.

13. Conclusions

This research aims to study hydro-geochemistry to assess the groundwater quality in the Wadi Al-Samen basin located in Hebron, West Bank.

It is also to understand the hydrological and chemical characteristics of the aquifer, and the need to develop future management plans to prevent the deterioration of groundwater in Wadi Al-Samen and to take appropriate decisions to reduce the extent degree of pollution because of the continuous flow of wastewater towards the valley. This study meets the needs of humans and farmers. To achieve the most prominent goal, geochemical parameters were studied and geospatial methods were combined to assess water quality by the water quality index (WQI).

The cation dominance pattern found in Wadi Al -Samen aquifer is Ca > Na > Mg > K. The prevalent tendency of the major anions in the Wadi Al-Samen aquifer is in the following order: Cl > HCO_3 > NO_3 > SO_4.

Through the classification of electrical conductivity (EC), the suitability of water quality for irrigation is assessed as one of the basic parameters for assessing the suitability of water quality for irrigation.

For the sodium absorption ratio (SAR), there are three samples (W17, W19 and W20) that are not suitable for irrigation. The Wilcox diagram is considered the main criterion for assessing the suitability of water quality for irrigation. It indicates that 85% of the water samples represent high salinity for irrigation with low sodium content.

The chemical properties of the wastewater components were studied to find out the composition, properties, and characterization of the pollutants in the area. The results of the analysis of sewage samples flowing in the valley indicated high levels of Biological Oxygen Demand (BOD_5) reaches 918 (mg O_2/l) in some areas, and high levels of Chemical Oxygen Demand (COD) reaches 1933 (mg/l). These values decrease in the winter season.

By evaluating the water samples chemically, the groundwater results indicated that it is not suitable for irrigation and drinking purposes, and needs treatment, as a result of the increase in nitrate levels in some samples, which is due to the presence of sewage water, and the increase in human activity in the area.

The results obtained from this study are very important in environmental integration for achieving sustainable groundwater management, mitigating the negative effects of sewage flow, and setting appropriate plans to avoid further deterioration of groundwater quality in the region, and an important basis for future studies.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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