Hydro-geochemistry and application of water quality index (WQI) for ground water quality assessment, Wadi Al-Samen –Hebron – West Bank

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Abstract

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 wasn't found unsuitable in three water resources samples. Wilcox analysis for the two seasons revealed that 85% of samples are not appropriate for irrigation uses.

Located south of the West Bank, Wadi Al-Samen is considered one of the most important sources of groundwater recharge. 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; geochemical methods were used for the sample result analysis. To characterize wastewater components, six samples were collected from the Wadi discharge for two seasons.

The results of nitrate levels showed that 20% of the 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$_4$. Rock interaction is a hydrochemical method for describing the main mechanisms that govern the chemistry of groundwater. The dominant hydrochemical facies of 35% of collected aquifer samples reveal that Ca-Mg-Na-Cl-HCO$_3$ are in the domain.

Introduction

To conduct comprehensive assessments of groundwater studies to assess its properties, geological, geochemical and geophysical data are used (Kotra et al., 2016). Geochemical exploration of groundwater is one of the most important methods used to identify patterns of mineralization (Hamzaoui-Azaza et al., 2020). The process of infiltrating groundwater to depth increases the chances of mineralization compared to surface geochemical methods (Leybourne, 2010).

Hydrochemical information closely contributes to developing an understanding of groundwater systems and tracing historical developments. The different techniques helped clarify the flow of groundwater systems, explain their origins, and recharge methods, and estimate different timelines (Glynn and Plummer, 2005).

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 (Leybourne, 2010). The possibility of groundwater penetration into the depths of the earth's crust increases the chances of discovering mineralization and Water rock interaction processes (Leybourne, 2010).

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 (Back and Hanshaw, 1971). 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 (Raju et al., 2015).

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. The particles in a groundwater sample represent the dissolved concentrations in it which determine the composition of the well and are viewed as an indicator and benchmark of groundwater quality (Blanchett et al., 2010). 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 (Karunanidhi et al., 2020). 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 (BGR, 2011).

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 (Koonce et al., 2006). 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 (Ojo et al., 2014). 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 (Li et al., 2014).

To understand groundwater patterns and verify the integrity of 20 water samples in the Wadi Al-Samen basin, collected from aquifers 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.

Study Area

Site description

Wadi Al-Samen area is located in Hebron city in the southern area of the West Bank (Fig. 1), 36 km south of Jerusalem city. The total area of the Hebron governorate is 1036 km²; 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-Saman, south of Hebron (ESCHIA report, 2013).

The environmental damage resulting from untreated sewage in Wadi Al-Samen is a serious issue (The World Bank, 2015). 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. 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 (PWA Library, 2002).

There is no effective wastewater system for industrial or household purposes in Hebron city (UNIP, 2002). 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 (Al-Heeh, 2018). The climate in Hebron city is affected by the Mediterranean Sea (Owaiwi and Awadallah, 2004).

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 (Fanack, 2018).

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 (Fig. 2). Stratigraphy and lithology of the Wadi al Samen Catchment showed that it contains sedimentary carbonate rocks from Albanians to Eocene age, according to (Zaarir, 2017) the study area in Hebron.

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 (SUSMAQ, 2002).

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-Fawwar1, AL-Fawwar2, Bani naim2, and Bani naim3 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 (Fig. 3) and (Fig. 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 (Fig. 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 (Qannam, 2003).

**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, Rihia and Al-Samu’) before 1967 which were also rehabilitated by the local authorities. The only aquifer well that reaches the deep aquifers (Fig. 5) is the Rihia well, with an extraction of 45m$^3$/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 (SUSMAQ, 2002).

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 657m at the beginning of drilled 715m. Additionally, the Samu’a well decreased in 2016 to 434m in comparison to 552m at the beginning of drilled. The piezometry to the lower well (Rihia), at the beginning of drilled 335m, remained at the same level with slight fluctuation.

25–30% of the annual volume of rainfall infiltrates goes to groundwater and the average rainfall is 492 mm/Year, yielding a runoff coefficient of 4.04%, in addition of 68.96% of the annual volume of rainfall evaporates directly from the ground (Abed Rabbo et al., 1999).

**Materials And Methods**

The methodological approach used in this study is shown in (Fig. 7) as a flow chart.

**Samples collection and analysis**

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 (Fig. 6). Samples were collected, preserved and prepared according to standard method of wastewater (APHA, 2017). Samples were analyzed for pH, EC, BOD$\textsubscript{5}$, COD, TSS, and TDS.

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 (Fig. 7). The EC, total dissolved solids (TDS), pH and Temperature were all measured onsite. These variables were measured using portable field instruments. At the time of sampling, the 1000L plastic bottles for chemical tests were thoroughly rinsed 2–3 times using the same groundwater.

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$_3^-$). Samples taken from the field were labeled and taken to the laboratory and stored at temperatures below 4°C.

To verify the results of analysis for all samples, the charge balance errors (%E) was calculated by the following formula (Hounslove1995).

$$%E = \frac{\Sigma C - \Sigma A}{\Sigma C + \Sigma A}$$

1

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 ≈ 2.05% < 5%).

**Hydro-chemical characterization**

**Conventional methods:** The determination of the hydrochemical processes of the aquifers of Wadi AL-Samen was obtained through the creation of the Piper scheme (Piper, 1944).
**Origin of mineralization:** The origin of groundwater is determined by establishing some correlations between the main ions that the water consists of, and this is critical in understanding the associated primary interactions. To understand the main mechanisms that control groundwater, Gibbs’ diagram was used. Additionally, to understand the origin of groundwater mineralization and the main mechanisms that govern groundwater in Wadi Al-Samen basin, the chemical water type was determined.

**Multivariate statistical methods:** Multivariate statistical methods are applied to monitoring data sets. The most common analysis method is hierarchical cluster analysis (HCA) (Popugaeva et al., 2019).

The hierarchical classification tree to represent dry season samples (Fig. 15), for wet season (Fig. 16). The physicochemical parameters were analyzed in 20 samples collected in 2019-2020 for two seasons; these variables (pH, T, TDS, EC, Na+, Ca2+, Mg2+, K+, Cl−, HCO3−, and SO42−) were successfully used in hierarchical cluster analysis (HCA).

**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) (Eq. (2)), Salinity (Wilcox diagram)

\[
SAR = \frac{Na}{\sqrt{\frac{Ca+Mg}{2}}}
\]

**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.

**Results And Discussion**

The steps of this research are summarized according to the scheme in (Fig. 8).

1. **Wastewater**

**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.

**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 (Fig. 6). 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.

**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 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).

**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.

**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. BOD$_5$ ranged between 241 to 918 mg/l in dry season and 213 to 698 mg/l in wet season.

**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.

2. **Ground water Hydrochemistry**

**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.

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.

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 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.

**Water Chemistry**

**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 (WHO, 2011). 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 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 (Table 1). Groundwater samples did not exceed the threshold of the WHO and the maximum allowable level is 200 mg/l.
Table 2
Summary of statistical calculations of chemical types for Wet Season from Wadi Al-Samen wells

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>EC</th>
<th>T</th>
<th>TDS</th>
<th>NO₃⁻</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>HCO₃⁻</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>7.3</td>
<td>380</td>
<td>18</td>
<td>240</td>
<td>34.5</td>
<td>10.69</td>
<td>18.3</td>
<td>1.561</td>
<td>58.3</td>
<td>87</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Max</td>
<td>7.9</td>
<td>2298</td>
<td>23</td>
<td>1304</td>
<td>546.9</td>
<td>240.8</td>
<td>84</td>
<td>176</td>
<td>19.808</td>
<td>186.9</td>
<td>754</td>
<td>22.9</td>
</tr>
<tr>
<td>Stand. dev</td>
<td>0.1928</td>
<td>478.845</td>
<td>1.538</td>
<td>263.307</td>
<td>56.723</td>
<td>16.946</td>
<td>40.748</td>
<td>23.15</td>
<td>174.83</td>
<td>3.781</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>7.67</td>
<td>1055.6</td>
<td>20.45</td>
<td>641.3</td>
<td>51.76</td>
<td>37.50</td>
<td>58.65</td>
<td>7.4499</td>
<td>134.5</td>
<td>277.13</td>
<td>15.51</td>
<td></td>
</tr>
<tr>
<td>Std. error</td>
<td>0.04</td>
<td>107.07</td>
<td>0.3439</td>
<td>58.878</td>
<td>12.684</td>
<td>3.7892</td>
<td>12.684</td>
<td>9.1116</td>
<td>186.9</td>
<td>754</td>
<td>22.9</td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>7.7</td>
<td>967</td>
<td>20.5</td>
<td>601</td>
<td>95.44</td>
<td>35.45</td>
<td>46.4</td>
<td>7.635</td>
<td>133</td>
<td>253.6</td>
<td>15.8</td>
<td></td>
</tr>
<tr>
<td>Variance</td>
<td>0.037</td>
<td>229293.8</td>
<td>2.366</td>
<td>69330.7</td>
<td>601</td>
<td>11</td>
<td>1.561</td>
<td>59.8</td>
<td>100.5</td>
<td>6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 from 1.561 to 19.808 with an average of 7.4499.

Major Anions

The most abundant anions are (HCO₃⁻, Cl⁻, SO₄²⁻ and NO₃⁻). 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 tables (4&5). Cl⁻ analysis for most of springs were higher than the allowed range (250mg/l) as some springs are saline springs that follow from shallower aquifers or at the land surface. NO₃⁻ also increased in (Al Fawwar 1, 2) (W11, W12), Khursa (W16) and Abdo (W17) (accepted limit 50mg/l), this because of wastewater stream and manmade pollution with excess quantities of fertilizers. Show anions concentrations during 2 seasons. (Fig. 9), (Fig. 10) Nitrates and salinity are the most frequently polluted groundwater (Troudi, 2020).

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 (Fig. 11); (Fig. 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⁺, HCO₃⁻, Ca²⁺, Cl⁻.
Cluster 2: consists of the most wells composed of the least mineralized with the enrichment of $\text{SO}_4^{2-}$.

For wet season:

Cluster 1: consists of the most mineralized wells with highly $\text{Na}^+$, $\text{HCO}_3^-$, $\text{Ca}^{2+}$, $\text{Cl}^-$.

Cluster 2: consists of the least mineralized wells with a slight enrichment in $\text{mg}^+$.

**Water Rock Interaction**

Gibbs diagrams were used to understand the mechanisms and processes that control the chemistry of groundwater. Gibbs diagrams are plotting according to the total dissolved solids (TDS) with ratio ($\text{Na}^+/(\text{Na}^+ + \text{Ca}^{2+})$) (Fig. 13a) and ratio ($\text{Cl}^-/(\text{Cl}^- + \text{HCO}_3^-)$) (Fig. 13b).

For two seasons, this graph is used to describe the origin dissolved components such as the rock weathering dominance, the evaporation dominance, and the precipitation dominance, a Gibbs diagram is used (Gibbs 1970).

According to the graph, the data of Wadi Al-Samen samples indicates that the chemical composition governed by evaporation and rock weathering.

The plot of $\text{Ca}^{2+}$ and $\text{SO}_4^{2-}$ shows that for water resources samples (Fig. 14), Gypsum is the source of calcium in the two samples close to the bisector line (1:1), while the three samples that are above the straight line, indicates the presence of excess in $\text{Ca}^{2+}$, which indicates precipitation of carbonates. Many samples under the line 1:1 this indicates a deficit in $\text{Ca}^{2+}$, suggesting carbonate precipitation.

Many samples are close to the bisector line (1:1) of sodium compared to chloride's plot (Fig. 15), where evaporation is an essential process in controlling the groundwater’s chemistry.

Mineral dissolution is an essential part of groundwater mineralization by ion exchange with minerals present in clay soils in aquifers as well as reverse ion exchange (Fig. 16).

The Scatter plots ($\text{Ca}^{2+} + \text{Mg}^{2+}$) vs. ($\text{HCO}_3^- + \text{SO}_4^{2-}$) indicate the presence of carbonate and silicate weathering (Fig. 17), this is observed in samples that lie below the line1:1 in (Fig. 17). Three samples at the upper of the line 1:1 indicate that the water samples are associated with carbonate rocks. Samples to the right of the 1:1 line indicate abundance of $\text{SO}_4^{2-} + \text{HCO}_3^-$ is a sign of silicate weathering.

**Geochemical Facies**

**Water Type**

**Water classification**

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, (Fig. 18). It showed samples from springs and wells in the two seasons (dry and wet) located in earth alkaline with predominant bicarbonate.

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-HCO3. 20% of the samples showed that water type of Ca-Mg-Cl-HCO3, 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.
Table 3  
The Water types for two seasons in Wadi Al-Samen Basin

<table>
<thead>
<tr>
<th>Dry Samples</th>
<th>water type</th>
<th>Wet Samples</th>
<th>water type</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1</td>
<td>Ca-Mg-Na-Cl-HCO3</td>
<td>W1</td>
<td>Ca-Mg-Na-Cl-HCO3</td>
</tr>
<tr>
<td>W2</td>
<td>Ca-Mg-Na-Cl-HCO3</td>
<td>W2</td>
<td>Ca-Mg-Na-Cl-HCO3</td>
</tr>
<tr>
<td>W3</td>
<td>Ca-Mg-Cl-HCO3</td>
<td>W3</td>
<td>Ca-Mg-Cl-HCO3</td>
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<td>W4</td>
<td>Ca-Mg-Cl-HCO3</td>
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<td>Ca-Mg-Cl-HCO3</td>
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<td>W5</td>
<td>Ca-Mg-Na-Cl</td>
<td>W5</td>
<td>Ca-Mg-Na-Cl</td>
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<td>W6</td>
<td>Ca-Mg-Na-Cl</td>
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<td>W7</td>
<td>Ca-Mg-Na-Cl</td>
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<td>Ca-Mg-Na-Cl-HCO3</td>
</tr>
<tr>
<td>W8</td>
<td>Mg-Ca-Na-Cl-HCO3</td>
<td>W8</td>
<td>Mg-Ca-Na-Cl-HCO3</td>
</tr>
<tr>
<td>W9</td>
<td>Ca-Mg-Na-Cl-HCO3</td>
<td>W9</td>
<td>Ca-Mg-Cl-HCO3</td>
</tr>
<tr>
<td>W10</td>
<td>Ca-Mg-Na-Cl-HCO3</td>
<td>W10</td>
<td>Ca-Mg-Na-Cl-HCO3</td>
</tr>
<tr>
<td>W11</td>
<td>Ca-Mg-Cl</td>
<td>W11</td>
<td>Ca-Mg-Cl</td>
</tr>
<tr>
<td>W12</td>
<td>Ca-Mg-Cl</td>
<td>W12</td>
<td>Ca-Mg-Cl-HCO3</td>
</tr>
<tr>
<td>W13</td>
<td>Ca-Mg-Na-Cl-HCO3</td>
<td>W13</td>
<td>Ca-Mg-Na-Cl-HCO3</td>
</tr>
<tr>
<td>W14</td>
<td>Ca-Mg-Cl-HCO3</td>
<td>W14</td>
<td>Ca-Mg-Cl-HCO3</td>
</tr>
<tr>
<td>W15</td>
<td>Ca-Na-Cl-HCO3</td>
<td>W15</td>
<td>Ca-Na-Cl-HCO3</td>
</tr>
<tr>
<td>W16</td>
<td>Ca-Na-Mg-NO3-Cl</td>
<td>W16</td>
<td>Ca-Na-Mg-NO3-Cl</td>
</tr>
<tr>
<td>W17</td>
<td>Ca-Na-Mg-Cl</td>
<td>W17</td>
<td>Ca-Na-Mg-Cl</td>
</tr>
<tr>
<td>W18</td>
<td>Ca-Cl</td>
<td>W18</td>
<td>Ca-Na-Mg-Cl</td>
</tr>
<tr>
<td>W19</td>
<td>Ca-Na-Mg-Cl</td>
<td>W19</td>
<td>Ca-Na-Mg-Cl</td>
</tr>
<tr>
<td>W20</td>
<td>Ca-Na-Cl</td>
<td>W20</td>
<td>Ca-Na-Mg-Cl</td>
</tr>
</tbody>
</table>

Water Quality Index

Estimation and mapping of water quality index

Water quality is evaluated in any given area by using physical, chemical and biological tests. 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 (Tyagi et al., 2013).

The first step in evaluating the water index begins by determining the necessary parameters as follows (pH, TDS, Cl⁻, SO₄²⁻, HCO₃⁻, NO₃⁻, Ca²⁺), then the weight (wi) is determined on the basis of (Mg²⁺, Na⁺ and K⁺). In addition, to assess their expected effects on primary health, So that the parameters are assigned a maximum weight of 5.

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 (Wi) of each parameter is computed using Eq. (3):

\[ Wi = \frac{w_i}{\sum_{i=1}^{n} w_i} \]
Where: \( wi \) is the weight of each parameter, \( n \) is the number of parameters, \( Wi \) is the relative weight. The WHO standards for each parameter are given in Table 4.

### Table 4

The weight and relative weight of each of the chemical parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>WHO Standard</th>
<th>Weight (( wi ))</th>
<th>Relative Weight (( Wi ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.5</td>
<td>4</td>
<td>0.117647059</td>
</tr>
<tr>
<td>TDS</td>
<td>1000</td>
<td>5</td>
<td>0.147058824</td>
</tr>
<tr>
<td>( \text{NO}_3^- )</td>
<td>50</td>
<td>5</td>
<td>0.147058824</td>
</tr>
<tr>
<td>( \text{Ca}^{2+} )</td>
<td>200</td>
<td>3</td>
<td>0.088235294</td>
</tr>
<tr>
<td>( \text{Mg}^{2+} )</td>
<td>50</td>
<td>3</td>
<td>0.088235294</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>200</td>
<td>3</td>
<td>0.088235294</td>
</tr>
<tr>
<td>K(^+)</td>
<td>30</td>
<td>2</td>
<td>0.058823529</td>
</tr>
<tr>
<td>( \text{HCO}_3^- )</td>
<td>280</td>
<td>1</td>
<td>0.029411765</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>250</td>
<td>3</td>
<td>0.088235294</td>
</tr>
<tr>
<td>( \text{SO}_4^{2-} )</td>
<td>250</td>
<td>5</td>
<td>0.147058824</td>
</tr>
<tr>
<td>Total</td>
<td>( \sum wi = 34 )</td>
<td>( \sum Wi = 1 )</td>
<td></td>
</tr>
</tbody>
</table>

During the third step, the quality evaluation scale \((qi)\) was calculated. For each parameter using Eq. (4):

\[
qi = \frac{Ci}{Si} \times 100
\]

4

Where: \( qi \) is the quality rating, \( Ci \) is the concentration of each chemical parameter in each water sample in milligrams per liter, \( Si \) is the WHO standard for each chemical parameter in mg/l.

For calculating the WQI, the SI is first determined for each chemical parameter using Eq. (5), which is then used to determine the WQI as per the Eq. (6):

\[
SIi = Wixqi
\]

5

\[
WQI = \sum SIi
\]

6

\( SIi \) is the sub-index of \( i \)th parameter, \( qi \) is the rating based on concentration of \( i \)th 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 (Fig. 19a), (Fig. 19b).
Table 5
Water quality index (WQI) rating of groundwater samples (Brown et al., 1970 & Ramakrishnaiah et al., 2009)

<table>
<thead>
<tr>
<th>WQI range</th>
<th>Type of water</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 50</td>
<td>Excellent water</td>
</tr>
<tr>
<td>50–100.1</td>
<td>Good water</td>
</tr>
<tr>
<td>100–200.1</td>
<td>Poor water</td>
</tr>
<tr>
<td>200–300.1</td>
<td>Very poor water</td>
</tr>
<tr>
<td>&gt; 300</td>
<td>Unfit for drinking</td>
</tr>
</tbody>
</table>

1.1 Water Resources suitability for different purposes

1.2 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.

Table 6
Classification of Todd (2007) for the tolerance of different types of crops by using the conductivity value (Todd, 2007)

<table>
<thead>
<tr>
<th>Crop division</th>
<th>Low salt tolerance crops</th>
<th>Medium salt tolerance crops</th>
<th>High salt tolerance crops. EC (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EC (µS/cm)</td>
<td>3000–4000</td>
<td>4000-10,000</td>
</tr>
<tr>
<td>Fruit crops</td>
<td>0-3000</td>
<td>Cantaloupe, Olive, Figs, Pomegranate</td>
<td>Date palm</td>
</tr>
<tr>
<td></td>
<td>Limon, Strawberry, Peach spricot, Almond, Plum Orange, Apple, Pear</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vegetable crops</td>
<td>3000–4000</td>
<td>4000-10,000</td>
<td>10,000-120,000</td>
</tr>
<tr>
<td></td>
<td>Green beans, Celery, Radish</td>
<td></td>
<td>Spinach, Garden beets</td>
</tr>
<tr>
<td>Field crops</td>
<td>4000–6000</td>
<td>6000-10,000</td>
<td>10,000–16,000</td>
</tr>
<tr>
<td></td>
<td>Field beans</td>
<td>Sunflower, Corn (field), Rice, Wheat</td>
<td>Cotton, Sugar beet</td>
</tr>
</tbody>
</table>

1.2 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 Eq. (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 Bîr 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).

Table 7
Classification of water for irrigation suitability based on SAR (USDA, 1954)

<table>
<thead>
<tr>
<th>SAR value</th>
<th>Irrigation suitability</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 10</td>
<td>Excellent</td>
</tr>
<tr>
<td>10–18</td>
<td>Good</td>
</tr>
<tr>
<td>18–26</td>
<td>Fair</td>
</tr>
<tr>
<td>&gt; 26</td>
<td>Poor</td>
</tr>
</tbody>
</table>
1.3 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) (Fig. 20). The rest of the study samples were described as unsuitable for cultivation (Wilcox, 1955), being in medium salinity (C2) and low sodium (S1) as shown in (Fig. 20).

Conclusion

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. This study provides important information about basic geological formation. 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.

SAR, three samples (W 17, W19, and W20) 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 (BOD5) reaches 918 (mg O2/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 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.

Declarations

Availability of data and materials

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Authors’ contributions

Waseem Al-Tamimi was responsible for writing the manuscript, sample collection, lab analyses, conceptualization, investigation, methodology, formal analysis. Fadoua Hamzaoui-Azaza was responsible for conceptualization, revising the analysis, and visualization. Marwan Ghanem was responsible for conceptualization, revising the text and geological part validation. Rachida Bouhallila was responsible for conceptualization and investigation, validation, and supervision. All authors read and approved the final manuscript.

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Compliance with ethical standards

Competing interests

The research is original and there is no conflict of interest.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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Figures

Figure 1

Location of Hebron District, Wadi Al-Samen Basin
Figure 2

Geological strata and cross-section of Hebron Governorate and the boundaries of Wadi Al-Saman basin

Figure 3

Geological strata and cross-section of Hebron Governorate and the boundaries of Wadi Al-Saman basin
Correlation between Al-Samu’a, Al-Rihiya, AL-Fawwar2 Wells

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Correlation between Al-Samu’a, Al-Rihiya, Bani Naim 2, Bani Naim 3 Wells

Figure 5
Piezometric maps

Figure 6

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Figure 7

Ground water samples in wadi al-Samen basin
Hydro-chemical assessment of Wadi Al-Samen aquifer for Human consumption and agriculture Purposes

Study of the site

Geological and Hydrogeology

Wastewater sample

Chemical characterization (BOD, COD, TSS, TDS, EC, pH)

Water sample collection

In field measurement (EC, T, pH)

Lab

Chemical analysis

Ionic balance

Yes (<5%)

NO (>5%)

Conventional method (piper diagram)

Origin of mineralization

Multivariate statistical methods

Hydro-chemical facies identification

Hydrochemical characterization

Water quality

Drinking

Irrigation

WQI

EC

SAR

Salinity

Gis

Create thematic map

Interpretation and results

Figure 8

Flowchart illustrating the methodology applied for evaluation of groundwater of Wadi Al-Samen
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NO$_3^-$ concentrations for all samples in two rounds

Figure 10

Cl$^-$ concentrations for all samples in two rounds
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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

Gibbs diagram for Wet season in excel sheet (a) \((\frac{Na^+}{Na^+ + Ca^{2+}})\)(mg/L) vs (TDS mg/L) and (b) \((\frac{Cl^-}{Cl^- + HCO_3^-})\)(mg/L) vs (TDS mg/L)

Figure 14

Plot of \(SO_4^{2-}\) against \(Ca^{2+}\)
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Figure 16
Plot of Na\(^+\) against (Ca\(^+\)+Mg\(^+\))
Figure 17

Plot of (HCO$_3^-$ + SO$_4^{2-}$) against (Ca$^{2+}$+Mg$^{2+}$) in (mg/l) aquifer water samples

Figure 18

Piper Diagram for two seasons of Wadi al-Samen Basin
Figure 19

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Figure 20

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