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**THE ENVIRONMENTAL IMPACT OF THE PRODUCED WATER ON
THE UPPER AQUIFER IN THE WAHAT REGION, SIRT
BASIN, LIBYA**

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Abstract:

This paper based on data analysis by the Waha Oil Company of water samples collected from groundwater samples and produced water from Wahat region, Sirt Basin in Libya. This study provides a new pattern in the analysis of geochemical data which are in the form of a set of major ions and parameters such as acidity (pH), Total Solids Dissolved (TDS), total hardness of water (TH), the Residual Sodium Carbonate (RSC), Electrical Conductivity (EC), Magnesium Adsorption Ratio (MAR), the Kelly Ratio (KR), the permeability Index (PI), the Corrosivity Ratio (CR) and Total Organic Carbon (TOC). All that was performed using the statistical and analytical methods of data, and linking the results and information with each other will provide information on the sources of these elements and the water, also evaluate the water quality and suitability for drinking or irrigation. Based on the concentrations of the measure ions in the studied waters were ranged between desired range and the permissive range according to the World Health Organization. It appears that pH values of the groundwater are located within the safe range for drinking. To keep track of the suitability of the water for irrigation and drinking some of the important parameters and indicators used such as (RSC), (EC), (MAR), (KR), (PI), and (CR). Groundwater has been classified and showed that the water samples are classified as type (CaMgCl), while the produced water samples were classified as (NaCl).

Keywords: *Geochemical analysis, Groundwater, Libya, Pollution, Produced water, Wahat Region.*

INTRODUCTION

The environmental pollution is the interruption on environment system due to of the natural or anthropological activities, which destruct the environmental components such as air, water and soil. The pollution is one of the most serious challenges to scientists today as it has a negative impact on human and animal lives, hence this fact pushes the social and governmental organizations to focus their efforts to save the environment by education people via different sorts of public media and make possible all attempts to sustain the environment. This paper focusing on the negative impact of the surrounding oil fields to the Wahat (Oases) region, in particular Gialo, where produced water is spilled out in some places and hence polluted the surrounding environment where very sensitive desert plants are growing, which need special care to reduce any possible contamination. Similarly, the sensitive animals inhabit this arid to semiarid areas such as the study area. Due to the presence of several oil fields in the Wahat region (which covering an area of 2600 km²) and witnesses the drilling of the first

Oil Well in Libya in 1958. Since that time the oil activities in forms of exploration, production, and development wells as well as pumping stations, oil tanks, pipe lines and produced water basins, in addition to the residual products from the oil/gas/water separators are increased in number. Which ultimately resulted in incorporate huge amount of pollutants such as hydrocarbons, heavy metals and radioactive elements? The impact of the produced water in Wahat region (i.e. Galo-Awjila- Ajkharah) is not according to what addressed by the international rule in discharging produced water.

As well as, to expose the effects of the produced water on the Wahat region which are ignoring the well-known environmental rules in the discharging or recycling operations to eliminate the produced water impact. Accordingly, the researchers should assess both the produced water and the groundwater in Wahat region in order to find the possible scientific solutions for sustaining the environment.

OBJECTIVES

- 1- Determine the different pollutants which are infiltrated from Oil fields to groundwater.
- 2- Inspect the impact of the oil pollution on groundwater of Wahat region, with particular attention on Galo.

LOCATION

The geochemical data used in this study are obtained from geochemical analyses performed in 2009 by Waha Oil Company, (6 samples from produced water samples; 3 samples from shallow groundwater; and 2 from deep groundwater) as indicated in (Fig. 1).

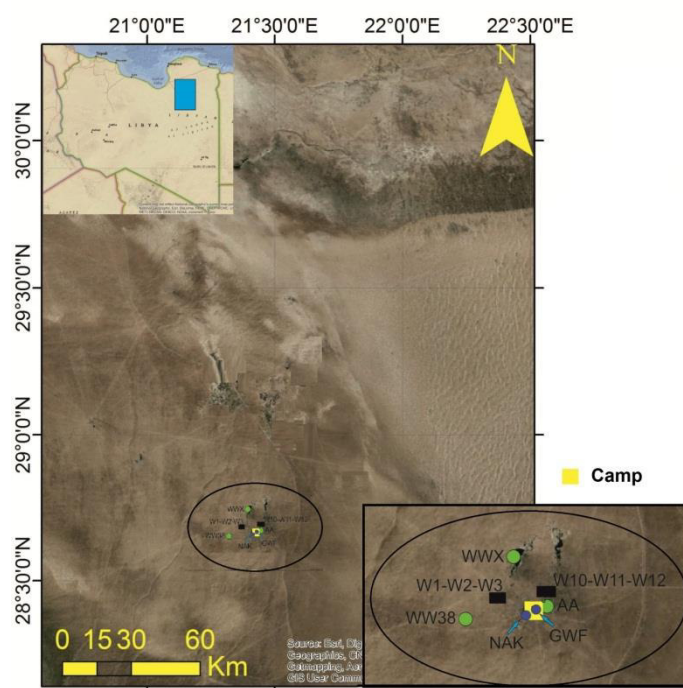


Figure 1: Location map of the analyzed water samples in 2009 from Wahat region, Libya.

GEOLOGICAL SETTINGS

The study area is located in largest sedimentary basin of Libya, which called Sirt Basin which has an area of 400.000km², and extending towards northwest-southeast as well as northward to the Mediterranean Sea. The Basin is architecture by faulting system with two major trends (NW-SE and E-W). The basin was formed between the beginnings of Late Cretaceous to the Early Miocene [1]. The study area is located in the northeastern part of Kalanshiyu province, which is the largest underground water region in Libya and seems to

be hexagonal in shape and bound an area of 375.000 km², this province linked geologically with Sirt Basin via post-Eocene aquifer network, it consists of continental sands, clays in the southern part, but marine carbonates with evaporates in the north. There is large amount of stagnant and clean underground water with salty water which is partly linked to rainy seasons during (Pleistocene age) when the province was under high moisture climate.

STRATIGRAPHY OF THE STUDY AREA

Important previous studies in the study area were summarized from the results of drilled water wells and exploration wells, and reports of consultants, including [2] from the British Geological Survey (IGS, 1982), and the French Giffley [3], from which a group of geological strata was identified and acting as underground water reservoirs extending from Al-Sarir area to the north of the study area.

The penetrated sequence of this region consists of sandstones and loose sands intercalated with clay and limestone, in addition to some evaporitic rocks (Fig. 2). According to what presented in an unpublished report about the water assessment in the Galo / Awjilah region (2002) the sequence from bottom to top as follows:

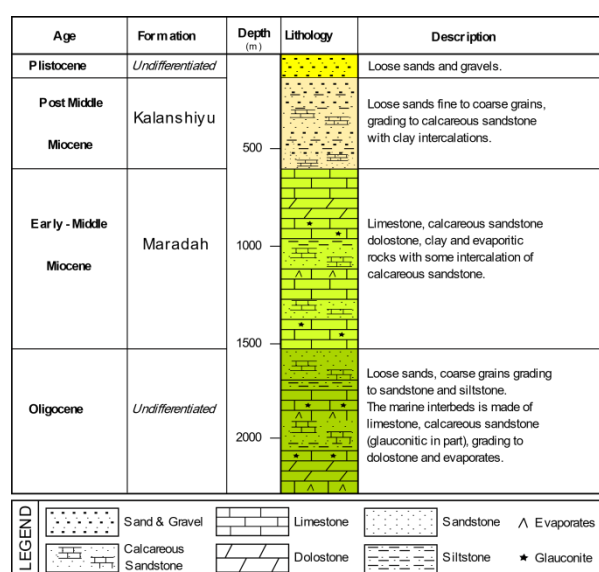


Figure 2: Lithostratigraphic Column of the Study Area.

Oligocene Interval (lower part): This interval consists of inter bedded coarse-grained sands to sandstone and siltstone reflecting the continental pulses of deposition. However, the marine intercalation of limestone and calcareous and glauconitic sandstones grading to dolostone with few evaporitic rocks are also presents. with thicknesses ranging from 242-697 meters depending on the site.

Previous studies showed that the water in this Oligocene reservoir is highly saline northwards including the oases area.

Maradah Formation (Early-middle Miocene): Maradah Formation in this study consists of limestone, sandy limestone, dolostone with a few clay and shale, which increase in importance in the southwest of the Sarir region with a thickness ranging between 121 - 697 m. The previous studies showed that there are hydraulic connections between the underground reservoirs in the area, as indicated by the leakage from bottom to top or sideways due to pressure contrast. The Groundwater flows from the south to the north / northeast in the direction of the topographical depressions of the oases following the hydraulic slope of 0.3%, and the water continues to flow northward until it intersects with subakhs in south of Jabal Al Akhdar and Sirt.

The near surface arrival of groundwater at the depressions allows the accumulation of salts as a result of evaporation and transpiration processes due to the hot dry climate in the oases region. The Oligocene reservoirs and the lower- middle Miocene reservoir contain high salinity water in several locations.

Kalanshiyu "calinchio" Formation (post- middle Miocene): It consists of medium grained sands with some fine and coarse grains locally becoming sandstones with thin intersections of clay with thicknesses up to 182m. This formation contains the first reservoir, which consists of the upper part of the Kalanshiyu Formation (upper sandstone) and the lower part represented by the formation formerly known as the Akalash Formation, whose importance lies north of the 29° line. The Institute of Geosciences and Scientific (IGS), according to According to Wright [2] reported that the post- middle Miocene reservoir increases in thickness from west to

east in the study area by an amount ranging between 75 - 115m. Since the maximum recorded thickness is to the North of the Concession-103 Oil Field.

Kalanshiyu "Calinchio" Formation (the upper part): This interval consists of fine to coarse loose sands and coarse-grained surface sand interbedded with clay and sometimes sandy limestone. The thicknesses are ranging from 0 to 30m. This interval of the formation contains the Kalanshiyu reservoir (the upper part). This aquifer is usually reached in all water produced drilled wells.

PRODUCED WATER

Produced water is low in the beginning of the operation processes and gradually increases with the continuation of production over time. For example, studies conducted in the North Sea by TotalFinaElf, [4] indicated that the quality of marine water can deteriorate with an area estimated at about 10 km² from drainage points and produced waters usually have a greater density than marine waters because they contain metal ions and contain small quantities of hydrocarbon. However, they are self-degrading by bacteria, wave movement and sunlight, and thus their environmental impact can be considered spatially limited [4]. On the other hand, most of the oil-producing companies in the oil fields surrounding the study area "Al-Wahat" relied on dumping the produced water in the adjacent sand basins as a final destination.

GEOCHEMISTRY AND ENVIRONMENTAL GEOCHEMISTRY

Groundwater is a vital source of clean drinking and irrigation water. This is increasingly the case due to the effects of population growth and climate change, which are causing severe stress to surface water supplies in these areas [5, 6]. The chemical composition of groundwater is controlled by several factors that include composition of precipitation, anthropogenic activities, geological structure and mineralogy of the watershed and aquifers and geological processes within the aquifer medium [7]. Chemistry of groundwater is an important factor determining its use for domestic and irrigation purposes. Interaction of groundwater with aquifer minerals through which it flows greatly controls the groundwater chemistry. Hydrogeochemical processes that are responsible for altering the chemical composition of groundwater vary with respect to space and time. The hydrogeochemical processes of the groundwater system help to obtain an insight into the contributions of rock and soil–water interaction and anthropogenic influences on groundwater. These geochemical processes are responsible for the spatiotemporal variations in groundwater chemistry [8,9,10]. Groundwater chemistry, in turn, depends on a number of factors, such as general geology, degree of chemical weathering of the various rock types, quality of recharge water and inputs from sources other than water–rock interaction [10, 11,12,13]. The quality of ground water is the resultant of all the processes and reactions that have acted on the water from the moment it condensed in the atmosphere to the time it is discharged by a well. Therefore, the quality of ground water varies from place to place, with the depth of water table, and from season to season and is primarily governed by the extent and composition of dissolved solids present in it. Worldwide, aquifers are experiencing an increasing threat of pollution from urbanization, industrial development, agricultural activities and mining enterprises. In recent years, an increasing threat to ground water quality due to human activities has become of great importance [14]. The chemical analysis of the studied water samples includes a group of major ions such as Ca⁺, Na⁺, K⁺, Fe⁺, Mg²⁺, Cl⁻, HCO₃⁻ and SO₄²⁻ (Tables 1-3). The pH values range from 6.95 to 7.60 in the produced water, from 6.89 to 7.60 in the shallow water and from 7.44 to 7.54 in the deep water indicating acidic conditions. Differences in chemical composition of the studied water samples suggest different sources of the major ions. The sources of these ions could be natural or anthropogenic.

Table 1: Chemical analysis data (concentration in mg/l) of the studied produced water samples

Sample No.	W1	W2	W3	W10	W11	W12
pH	7.60	7.35	7.35	7.15	6.95	7.30
K	200.00	226.00	216.00	510.00	360.00	342.00
Ca	640.00	816.00	800.00	3280.00	2280.00	1840.00
Na	6000.00	9100.00	7700.00	20400.00	16000.00	13700.00
Mg	216.00	326.40	230.40	566.40	436.80	403.20
Cl	8997.20	13695.75	13525.81	39987.60	24626.00	24992.25
HCO ₃	884.50	732.00	610.00	610.00	701.50	915.00
SO ₄	2276.00	3392.00	386.00	1600.00	1400.00	472.00
SO ₃	1897.00	2827.00	322.00	1333.00	167.00	393.00
Br	0.41	0.42	0.13	0.36	0.22	0.36
TOC	3.30	3.50	1.70	0.90	1.40	0.80
TDS	19317	27975	24438	27055	27165	43103

Table 2: Chemical analysis data (concentration in mg/l) of the studied shallow water samples

Sample No.	AA	WW38	WWX
pH	7.60	7.51	6.89
K	24.00	56.00	32.00
Ca	272.00	624.00	184.00
Na	450.00	610.00	420.00
Mg	105.60	129.60	67.00
Cl	989.69	819.75	909.72
HCO ₃	122.00	152.50	30.50
SO ₄	612.00	2123.00	367.00
SO ₃	510.00	1769.00	305.00
Br	0.18	0.27	0.65
TOC	0.00	0.00	0.00

Schoeller [15] diagram provides a convenient way to present chemical composition of groundwater of a region. In the present study, plots of average composition in mg/l are presented in Fig. (3). The relative tendency of ions in mg/l shows $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$ and $\text{Cl} > \text{SO}_4 > \text{HCO}_3$. The average ionic composition of groundwater is also represented by Stiff diagram. The shape analysis of stiff diagram signifies dominance of Na-Cl, while Ca-HCO₃ and Mg-SO₄ are nearly equal in proportion.

Table 3: Chemical analysis data (concentration in mg/l) of the studied deep-water samples

Sample No.	GFW	NAK
pH	7.54	7.44
K	30.00	32.00
Ca	224.00	280.00
Na	390.00	530.00
Mg	110.40	105.60
Cl	869.73	1169.64
HCO ₃	152.50	152.50
SO ₄	541.00	533.00
SO ₃	450.00	444.00
Br	0.04	0.09
TOC	0.00	0.00

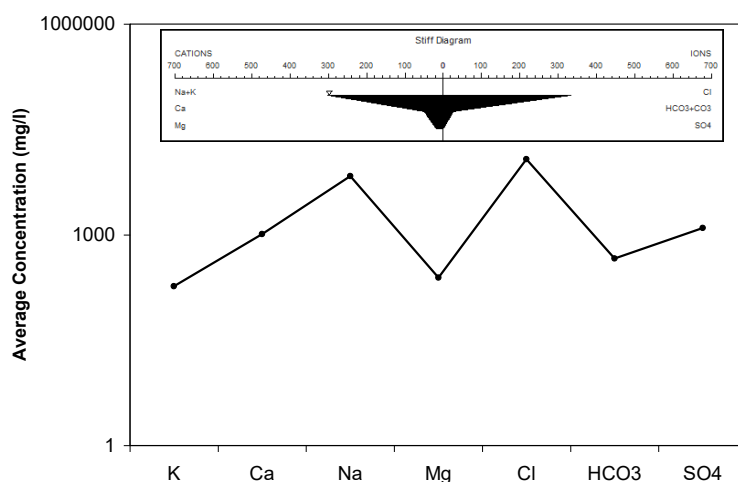


Figure 3: Schoeller diagram showing average composition of the studied water samples. Stiff diagram is shown in inset.

Statistical treatment

The statistical treatment of the obtained data involves descriptive statistics and correlation matrix using the SPSS[®] program (Tables 4-5). The correlation matrix suggests that the analyzed ions are possibly of common source (except SO₄).

Table 4: The descriptive statistics of the studied water samples (concentration in mg/l)

Ions	N	Min	Max	Mean	Std. Deviation
K	11	24.00	510.00	184.36	166.48
Ca	11	184.00	3280.00	1021.82	1009.87
Na	11	390.00	20400.00	6845.45	7236.51
Mg	11	67.00	566.40	245.22	165.76
Cl	11	819.75	39987.60	11871.19	13175.57
HCO ₃	11	30.50	915.00	460.27	338.66
SO ₄	11	367.00	3392.00	1245.64	1005.14

Table 5: Correlation matrix of the studied water samples

Ions	K	Ca	Na	Mg	Cl	HCO ₃	SO ₄
K	1.00						
Ca	0.95	1.00					
Na	0.99	0.96	1.00				
Mg	0.99	0.96	0.99	1.00			
Cl	0.99	0.97	0.99	0.98	1.00		
HCO ₃	0.78	0.58	0.76	0.74	0.70	1.00	
SO ₄	0.26	0.16	0.24	0.31	0.18	0.41	1.00

Sources

In the present study, the Cl/Na ratio is more than 1.17 in all the studied water samples (Tables 6-8). According to Shaltami [16] the calculation of none sea salt sulfate (nss-SO₄) values is based on equations as follows:

1) If Cl/Na ratio > 1.17

$$\text{nss-SO}_4 = [\text{SO}_4]_{\text{sample}} - [\text{Na}]_{\text{sample}} \times [\text{SO}_4/\text{Na}]_{\text{seawater}}$$

2) If Cl/Na equivalent ratio < 1.17

$$\text{nss-SO}_4 = [\text{SO}_4]_{\text{sample}} - [\text{Cl}]_{\text{sample}} \times [\text{SO}_4/\text{Cl}]_{\text{seawater}}$$

Table 6: Ratios of major ions in the studied produced water samples

Sample No.	W1	W2	W3	W10	W11	W12
Cl/Na	1.50	1.51	1.76	1.96	1.54	1.82
nss-SO ₄	1916.00	2846.00	76.00	376.00	440.00	350.00
nss-SO ₄ /Na	0.32	0.31	0.01	0.02	0.03	0.03
K/Na	0.03	0.02	0.03	0.03	0.02	0.02

Table 7: Ratios of major ions in the studied shallow water samples

Sample No.	AA	WW38	WWX
Cl/Na	2.20	1.34	2.17
nss-SO ₄	585.00	2086.40	341.80
nss-SO ₄ /Na	1.30	3.42	0.81
K/Na	0.05	0.09	0.08

Table 8: Ratios of major ions in the studied deep-water samples

Sample No.	GFW	NAK
Cl/Na	2.23	2.21
nss-SO ₄	517.60	501.20
nss-SO ₄ /Na	1.33	0.95
K/Na	0.08	0.06

According to El-Omla and Aboulela [17] there are three main origins for dissolved solids in waters: marine, anthropogenic and terrigenous. Sodium is generally considered as a tracer of the marine source, although a small contribution of terrigenous origin arises due to the input of crustal aerosols [18, 19]. The source of sulfate is complicated, as it also has a marine origin [20, 21]. Consequently, these ions are used to identify the sources of the dissolved solids in the studied water samples.

In the studied samples, the very strong correlation between Na and Cl ($r = 0.99$, Fig. 4) is valuable to appraise relation with seawater. The Cl/Na ratio ranges from 1.34 to 2.23, all slightly higher than the average seawater value (Cl/Na=1.17). Since the existence of the abundant nss-SO₄ indicates an anthropogenic origin, waters with a Cl/Na ratio larger than 1.17 may have not only marine and terrigenous but also anthropogenic origins. In agreement with [16] this assumption seems to be eligible for the studied waters as confirmed by the negative weak correlation between the Cl/Na ratio and the nss-SO₄/Na ratio ($r = -0.09$, Figure 5).

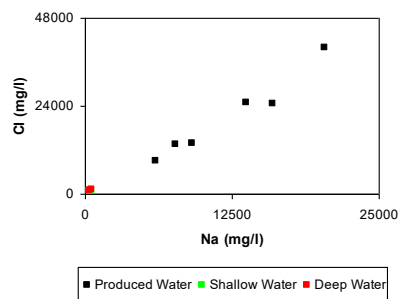


Figure 4: Relationship between Na and Cl in the studied water samples

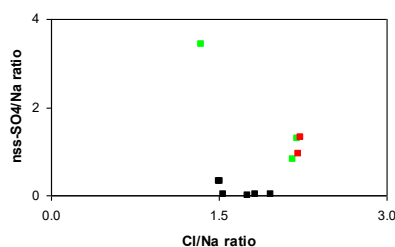


Figure 5: Relationship between Cl/Na and nss-SO₄/Na ratios in the studied water samples
(For legend see figure 4).

In the present study, K is strongly correlated with Na ($r = 0.99$, Fig. 6), suggests the same or similar origin of K and Na, while it is weakly correlated SO₄ ($r = 0.26$, Fig. 7), suggesting a different origin. According to [10] the main sources of K in ground water include rain water, weathering of potash silicate minerals, use of potash fertilizers and use of surface water for irrigation.

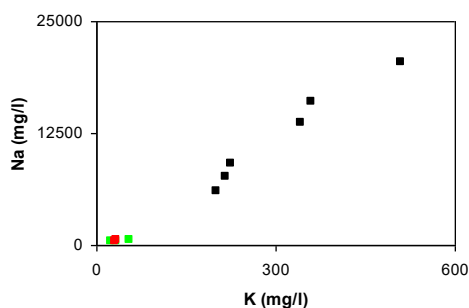


Figure 6: Relationship between K and Na in the studied water samples
(For legend see figure 4).

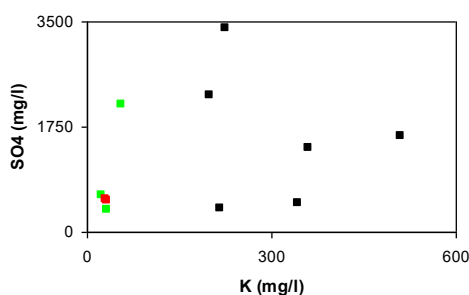


Figure 7: Relationship between K and SO₄ in the studied water samples

The molar $\text{Na}/\text{Na}+\text{Cl}$ and $\text{Ca}/\text{Ca}+\text{SO}_4$ ratios are imperative to relate the genetic relationship [22]. Groundwater of the study area show that majority of the samples are in the alignment from seawater to domain of evaporation (Fig. 8). The influence of evaporation in the study area also show compatibility with [23] work, indicating high ionic $\text{Cl}+\text{SO}_4$ balance (13116.83 mg/l) in contrast to HCO_3 (460.27 mg/l) in the groundwater.

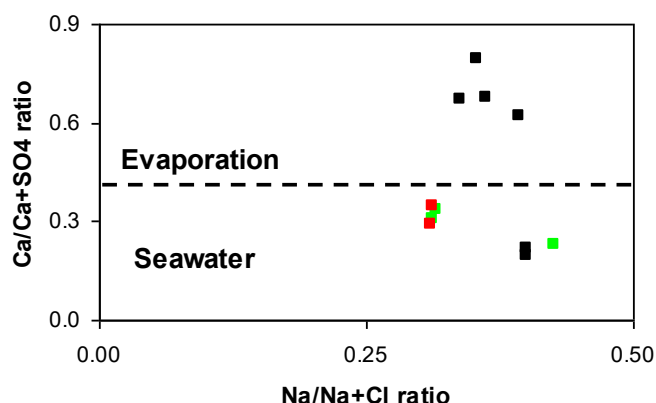


Figure 8: Molar $\text{Na}/\text{Na}+\text{Cl}$ and $\text{Ca}/\text{Ca}+\text{SO}_4$ to differentiate water of different origin (fields after [22]). (For legend see Figure 4).

The concentration of SO_4 in the studied samples ranges from 367 to 3392 with a mean concentration of 1245.63 mg/l. Sulfate do not demonstrate any confident coherence to any of the analyzed major ions. Water containing more than 1000 mg/l sulfate are harmful for plants [24].

Chloride ion up to 70mg/l is considered safe [25]. It causes severe problem in the crops at concentration > 350 mg/l [26]. The content of Cl in the groundwater is best to study water-rock interaction. Groundwater having more HCO_3 and less Cl ions is the indication of natural water with no influx of pollution [27]. In the studied samples, the Cl concentration is much higher than the HCO_3 concentration. The average HCO_3/Cl ratio is valuable to discriminate either seawater intrusion or rock weathering [28]. The HCO_3/Cl ratio of study area, except the produced water samples, is much higher than the average seawater ratio (0.004). Probably the high ratio is due to the weathering of rocks. Mutual relationship of $\text{Cl}/\text{Cl}+\text{HCO}_3$ vs. logs TDS in form of [29] diagram signifies dominance of evaporation in the studied produced water samples (Figure 9).

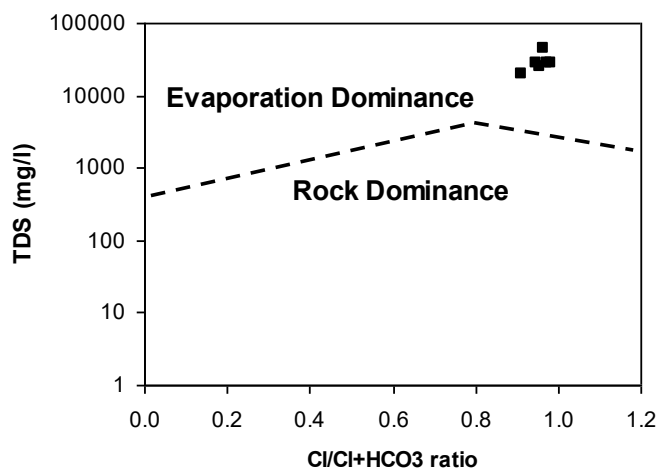


Figure 9: Dominance of rock and evaporation on $\text{Cl}/\text{Cl}+\text{HCO}_3$ vs. log TDS of the study area (fields after [29]) (For legend see figure 4).

The Ca and Mg ions are significant to appraise the magnitude of seawater contribution. The low Ca/Mg ratio (0.3) may indicate seawater influence [30]. In the studied water samples, Ca is strongly correlated with Mg ($r = 0.96$, Fig. 10), suggests the same origin of Ca and Mg. The Ca/Mg ratio ranges from 2 to 5.79, indicating, in agreement with [25], complexity in the budget of Ca and Mg of groundwater due to interaction with rocks and the arid climate of the study area. The $\text{Ca}+\text{Mg}-\text{HCO}_3$ in the present study range between 28.5 to 3236.4 with a mean of 938.18 indicating that Ca and Mg are driven from different sources.

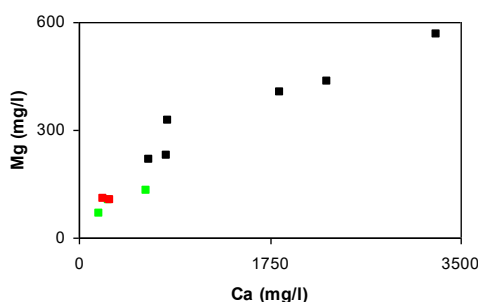


Figure 10: Relationship between Ca and Mg in the studied water samples
(For legend see figure 4).

DRINKING WATER QUALITY

Power of hydrogen (pH): The pH of drinking water is an important parameter and may affect health of humans. The studied water samples display pH within a range of 6.89 to 7.60 with a mean 7.32, indicating all samples are suitable for drinking purpose as recommended by World Health Organization (WHO [31]).

Total Dissolved Salts (TDS): In the produced water samples, TDS ranges between 19317 to 43103 mg/l with a mean of 28934 mg/l. All the produced water samples are over the safe limit (500 mg/l, by WHO, [31]).

Sodium (Na): The studied water samples display Na within a range of 390 to 20400 mg/l with a mean 6845.45 mg/l. All the water samples are over the safe limit (200 mg/l, by [31]). It is important to note that ~50 mg/l is desirable for human consumption [31]. High amount of Na in the drinking water has been linked to hypertension, cardiovascular disease, kidney damage, and calcium retention and bone density [32]. It regulates electrolytic balance in the human body and helps to transmit nerve impulses. Approximately 98% sodium is absorbed in the intestine, and excess sodium is excreted mainly by the kidneys with some loss occurring in sweat. In healthy adult humans at steady state conditions, urinary sodium excretion roughly equals to intake [33].

Potassium (K): The abundance of K in the waters of the study area varies between 24 to 510 mg/l with an average of 184.36 mg/l. The studied waters (except the produced water samples) are below the safe limit (100 mg/l, [31]). Potassium, the third most abundant mineral in human body, is the synonym for health insurer. Apart from acting as an electrolyte, K is required for keeping heart, brain, kidney, muscle tissues and other important organs of human body in good condition. High-K may also prevent or at least slow the progression of renal disease [34]. An increased K intake lowers urinary calcium excretion and plays an important role in the management of hypercalciuria and kidney stones and is likely to decrease the risk of osteoporosis. Low serum K is strongly related to glucose intolerance, and increasing K intake may prevent the development of diabetes that occurs with prolonged treatment with thiazide diuretics [35].

Calcium (Ca): Calcium in the waters of study area varies from 184 to 3280 mg/l with the mean of 1021.82 mg/l. The desirable and permissible limit of Ca in the drinking water is 75 and 200 mg/l [31]. All the studied water samples are over the safe limit (except samples W12 and WWX). Calcium is the most abundant metal in the human body. Calcium is present in the human body in amounts of about 1.2 kg. It is the main constituent of bones and teeth and it has key metabolic functions. It also assists the functions of nerves and muscles. Lack of calcium is one of the main causes of osteoporosis. Osteoporosis is a disease in which the bones become extremely porous, are subject to fracture. Calcium is also present in muscle tissue and in the blood. It is required for cell membrane development and cell division, and it is partially responsible for muscle contractions and blood clotting [36]. In order to stimulate these body functions a daily intake of about 1000 mg of Ca is recommended for adults [34].

Magnesium (Mg): In the present study, the lowest content of Mg is noted as 67 mg/l, while highest amount is recorded as 566.4 mg/l. Drinking water having Mg content ~30 is best and up to 150 mg/l concentration it is considered safe for human health [31]. The studied waters (except the produced water samples) are below the safe limit. Magnesium in drinking water may have a laxative effect, particularly with MgSO_4 on concentration above 700 mg/l [34]. However, the human body tends to adapt to this laxative effect with time. Magnesium is responsible for the activation of enzymes, maintain muscle and nerve function in human body. Early signs of Mg deficiency include loss of appetite, nausea, vomiting, fatigue, and weakness [37]. As Mg deficiency worsens, numbness, tingling, muscle contractions and cramps. Severe Mg deficiency can result in low levels of Ca and K

in the blood [38]. Disease like hypertension, cholesterol level, type2 diabetes and cardiovascular disease can be control by taking high Mg [39].

Sulfate (SO₄): In the studied samples, the SO₄ values range from 367 to 3392 mg/l with a mean concentration of 1245.64 mg/l. [31] has established 200 and 600 mg/l as desirable and permissible limit in the drinking water. The studied waters (except the produced water samples and sample WW38) are below the safe limit. People not familiar to consume high levels of SO₄ ions can experience dehydration and diarrhea. Kids are often more sensitive to SO₄ than adults. Drinking high SO₄ containing water may cause laxative effect in human beings [40].

Chloride (Cl): The chloride concentration in the waters of the study area ranges from 819.75 to 39987.6 mg/l. These amounts are higher than desirable limit (250mg/l, by [31]). In humans, 88% of chloride is extracellular and contributes to the osmotic activity of body fluids. The electrolyte balance in the body is maintained by adjusting total dietary intake and by excretion via the kidneys and gastrointestinal tract [34]. Chloride is almost completely absorbed in normal individuals, mostly from the proximal half of the small intestine. Normal fluid loss amounts to about 1.5-2 liters/day, together with about 4 g of chloride per day. Most (90-95%) is excreted in the urine, with minor amounts in faeces (4-8%) and sweat (2%) [41]. Chloride toxicity has not been observed in humans except in the special case of impaired NaCl metabolism, e.g. in congestive heart failure. Little is known about the effect of prolonged intake of large amounts of chloride in the diet [42].

Bicarbonate (HCO₃): The quantity of HCO₃ ions in the water samples of study area ranges between 30.5 to 915 mg/l. [31] has established 300 and 600 mg/l as desirable and permissible limit in the drinking water. The studied waters (except the produced water samples) are below the safe limit. Bicarbonate is a major ion in our body, secreted by the stomach, it is necessary for digestion. When ingested, for example, with mineral water, it helps buffer lactic acid generated during exercise and also reduces the acidity of dietary components. Finally, it has a prevention effect on dental cavities. The most important effect of bicarbonate ingestion is the change in acid-base balance as well as blood pH and bicarbonate concentration in biological fluids. High HCO₃ bearing water is useful in the prevention of the recurrence of calcium oxalate and uric acid renal stones [43].

Total Hardness (TH): Water hardness is the measure of the ability of water to react with soap and produce froths. It is based on Ca and Mg salts and can be calculated as follows:

$$TH \text{ (mg/l CaCO}_3\text{)} = 2.5 \text{ Ca (mg/l)} + 4.1 \text{ Mg (mg/l)}$$

In the studied water samples, TH ranges from 734.7 to 10522.24 with a mean of 3559.94 mg/l. [44] permit maximum 500 mg/l standard for drinking purposes. All the studied water samples have TH exceeding the maximum allowable limit. Both Ca and Mg are essential minerals for human health, deficiency or excess can result in adverse health consequences. Continuous use of hard water may cause cancer, cardiovascular disease, urolithosis and another kidney ailment [45].

IRRIGATION WATER QUALITY

Power of hydrogen (pH): The pH is one of the most important factors influencing the suitability of water for irrigation purpose. The normal pH range for irrigation water is from 6.5 to 8.4 [46]. The water samples of the study area within a range of 6.89 to 7.6 with a mean 7.32, indicating all samples are suitable for irrigation purpose.

Residue Sodium Carbonate (RSC): Residual sodium carbonate (RSC) exists in irrigation water when the carbonate (CO₃) plus bicarbonate (HCO₃) content exceeds the calcium (Ca) plus magnesium (Mg) content of the water [47]. RSC is a significant factor that has a great influence on the suitability of water for irrigation purposes. It is estimated from the following expression:

$$RSC = [(HCO_3) + CO_3] - [Ca + Mg] \quad (\text{all concentrations are expressed in meq/l})$$

When the RSC value is lower than 1.25meq/l, the water is considered good quality, while if the RSC value exceeds 2.5meq/l, the water is considered harmful. The samples of the study area have RSC between -177.77 to -0.09, indicating good quality water for irrigation purpose. Continuous use of waters having RSC more than 2.5 meq/l leads to salt build up which may hinder the air and water movement by clogging the soil pores [48].

Sodium Percent (Na %) and Electrical Conductivity (EC): Johnson and Zhang [49] used total salt (EC) and Na% to classify the irrigation water into six classes. Total salt concentration (i.e. salinity) is the sum of cations plus anions. The Na in irrigation waters is usually refers as Na percent and determined using the given equation [50].

$$\text{Na\%} = (\text{Na}^+ * 100) / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+) \quad (\text{all concentrations are expressed in meq/l})$$

Irrigation water with Na% > 60% may result in Na accumulation and possibly a deterioration of soil structure, infiltration, and aeration [51]. Figure (11) shows that the shallow and deep waters are classified as good, while the produced waters are classified as very poor and unsuitable.

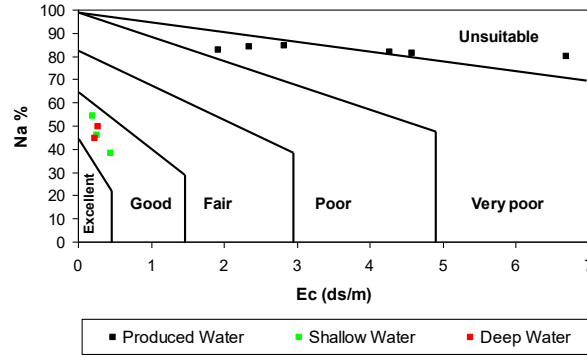


Figure 11: Classification of irrigation water on EC vs. Na% (Fields after [49])

Sodium Adsorption Ratio (SAR): The Na or alkali hazard is expressed in terms of sodium adsorption ratio [27]. Sodium adsorption ratio (SAR) is the measurement of Na content relative to Ca and Mg in soil-water phase which influences soil properties and plant growth. Sodium adsorption ratio (SAR) can be determined from the following expression:

$$\text{SAR} = \text{Na} / \sqrt{(\text{Ca} + \text{Mg})/2} \quad (\text{all concentrations are expressed in meq/l})$$

SAR values <10 is classified as excellent for irrigation. Values in between 10-18 are good, moderate 18-26 and >26 are hazardous. The studied shallow and deep waters display SAR values <10 (6.1 in average), while the calculated SAR values of the produced waters lie between 52.17 and 86.31 (>26), indicating that the shallow and deep waters are classified as excellent for irrigation, while the produced waters are hazardous.

Magnesium Adsorption Ratio (MAR): Likewise, sodium adsorption ratio (SAR), magnesium adsorption ratio (MAR) is also considered as one of the significant parameters to evaluate irrigation water quality. The magnesium hazard (MAR) of irrigation water is proposed by Szabolcs and Darab [52] and redefined by Raghunath [53]).

$$\text{MAR} = [\text{Mg}^{2+} / (\text{Mg}^{2+} + \text{Ca}^{2+})]100 \quad (\text{all concentrations are expressed in meq/l})$$

In the analyzed groundwater samples, the MAR values range from 22.35 to 45.1. According to Ayers and Westcot [54]) MAR values exceeding 50 is considered harmful and unsuitable for irrigation use and may causes infiltration problem.

Kelley's Ratio (KR): Kelley [55] and Paliwal [56] introduced an important parameter to evaluate irrigation water quality based on the level of Na measured against Ca and Mg. Waters with KR <1 are suitable for irrigation. The studied shallow and deep waters display KR values <1 (0.92 in average) indicating their suitability for irrigational uses, while the calculated KR values of the produced waters lie between 4.2 to 5.82.

Permeability Index (PI): Continuous use of high salt bearing irrigation water may reduce soil permeability [57](Singh and Singh, 2008). Such problem can be assessed by computing PI of the irrigation water from the expression, suggested by Doneen [58].

$$\text{PI} = [(\text{Na}^+ + \text{HCO}_3^-) / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+)] 100 \quad (\text{all concentrations are expressed in meq/l})$$

According to this classification, irrigation water with high permeability (>75%) is classified as class I; class II has permeability between 50-75%; while class III has permeability <25% and unsuitable for irrigation purpose

[59]. On the basis of PI classification, the shallow and deep-water samples are class II (PI ranges from 43.35 to 56.78), while the produced water samples belong to class I (PI ranges from 81.68 to 88.58).

Corrosivity Ratio (CR): It is the tendency of water to corrode steel pipelines during the transportation of irrigation water or deposition of scaling film on the pipes. Alkalinity, Ca, TDS, pH and temperature is mainly responsible for corrosion. According to Tripathi *et al.*, [60] the CR is expressed as:

$$CR = [135.5 Cl + 2(SO_4/96)] / 2[(HCO_3 + CO_3)/100] \quad (\text{all concentrations are expressed in meq/l})$$

The groundwater with corrosivity ratio < 1 is considered to be safe for transport of water in any type of pipes, whereas > 1 indicate corrosive nature and hence not to be transported through metal pipes [61]. All the studied samples show CR more than 1, which suggests that the analyzed waters are corrosive in nature and need non-corrosive pipe for transporting and lifting of groundwater.

Classification of water

Piper [62] classified water types and hydrogeochemical facies on the basis of major ion chemistry in groundwater flow systems. The shallow and deep-water samples of study area show distribution of mixed-type cations, while the produced water samples have influence of Na+K-type water on piper diagram (Fig. 12). Among the major anions, the studied water samples are plotted towards Cl-type. The hydrofacies analysis of the study area reflects that water originates in the close geological environment. Majority of the shallow and deep-water samples are plotted in the CaMgCl-type of water, while the produced water samples are plotted in the NaCl-type of water.

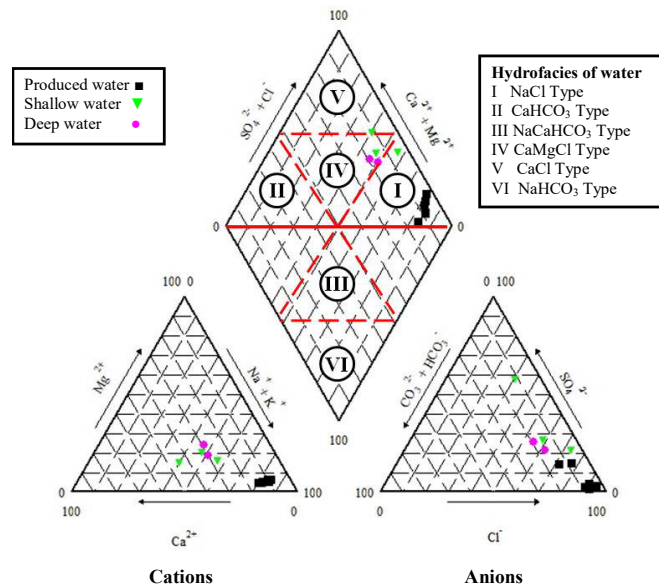


Figure 12: Piper diagram of groundwater chemistry in the study area (fields after Tweed *et al.*, [63])

RESULTS AND DISCUSSIONS

The chemical analysis of the analyzed water samples included a group of main ions such as calcium, sodium, potassium, iron, magnesium, chlorine, bicarbonate and sulfate. The pH values range between 6.77 and 7.60 in the studied water, indicating acidic conditions. The studied water samples showed that sodium > calcium > magnesium > potassium and chlorine > sulfate > bicarbonate. Stiff's diagram indicated the dominance of (sodium-chlorine), while roughly equal in the values of the ratios of (calcium-bicarbonate) as well as magnesium-sulfate. A strong relationship between sodium and chlorine ($r = 0.99$) is useful for assessing the relationship with seawater. The ratio of chlorine / sodium ranges between 0.75 and 18.51, while the average value of sea water is estimated at (1.17). The presence of an abundance of non-marine sulfate salts (nss-SO₄) indicates human origin, and the chlorine / sodium ratio greater than 1.17, which may not only be marine or continental, but even anthropogenic. This hypothesis seems valid for the studied samples as confirmed by the weak correlation between the ratio of Cl/Na and the ratio of (nss-SO₄ / Na $r = -0.27$). It may not be of marine and continental origin only, but also the result of industrial activity, and this may qualify for the studied water as indicated by the weak negative correlation between the chlorine / sodium ratio as well as the nss-SO₄ / sodium ratio ($r = -0.09$).

Potassium is strongly correlated with sodium ($r = 0.99$), indicating that the two have roughly the same or similar source, while it is poorly correlated to sulfate ($r = 0.39$) indicating different sources.

Groundwater in the study area was indicated that the vast majority of samples are located along the sea water to the evaporation field. The concentration of chlorine is much higher than that of bicarbonate, while the percentage of bicarbonate / chlorine in the study area (excluding the produced water samples 2009) is much higher than the average percentage of sea water (0.004). This high percentage is probably due to the weathering of the host rocks. The plotted values of the studied samples on the Gibbs graph indicated the predominance of evaporation in the produced water samples. Calcium is strongly correlated to magnesium ($r = 0.78$) indicating the same source for both. The ratio of calcium / magnesium ranges between 0.22 to 5.79, and this indicates the complexity in the calcium and magnesium budget of the groundwater due to the interaction of the groundwater with rocks and the arid climate of the study area.

In general, the total solid salts, total hardness, and the ratios of sodium, calcium and chlorine were above the safe limit, while the levels of potassium, magnesium, sulfate and bicarbonate in the studied water (excluding the produced water samples) were below the safe limit. While the pH within the safe range for drinking purposes.

The assessment of groundwater quality for irrigation purposes was carried out using various indicators such as Residue of Sodium Carbonate (RSC), which ranges between -177.77 to 0.4, indicated it is good for irrigation.

Based on the values obtained in this study for Electrical Conductivity (EC), Sodium Absorption Ratio (SAR), Magnesium Absorption Ratio (MAR), Kelly Ratio (KR) and Corrosion Ratio (CR), shallow and deep water are classified as good, however, the produced water is classified as very bad and unsuitable. Shallow water and deep water are classified as excellent for irrigation, while, the produced water is hazardous. According to the Permeability Index (PI), the produced water is classified as Class I, while shallow water and deep water are classified Class II.

All the studied samples showed that the Corrosivity Ratio is <1 , which indicates that the analyzed water is corrosive in nature and needs non-corrosive pipes to transport and raise the groundwater. According to the Piper diagram the shallow water samples and the deep-water samples for this study presented a distribution of mixed types of cations, while the produced water samples fall into (Na + K) type. However, anions of the studied water samples fall into (Cl) type. The hydrofacies analysis of the studied water showed that the water originates from its nearby geological environment. Most of the shallow and deep-water samples fall into (CaMgCl) type, while the produced water samples (2009) fall into (NaCl) type.

CONCLUSIONS

The current study concluded the followings:

1. The Power of Hydrogen pH, Residual Sodium Carbonate, magnesium absorption percentage and permeability coefficient indicate that all water is suitable for irrigation.
2. According to the Sodium Percent, the Electrical Conductivity and the Kelly Ratio, shallow and deep water are good for irrigation, while the produced water is not suitable for irrigation.
3. The Sodium Absorption Ratio indicates that shallow and deep waters are considered excellent, and produced waters are considered harmful.
4. The corrosivity Ratio is high in all the studied water, which indicates that this water causes corrosion of the pipes and therefore needs special pipes.
5. Piper diagram indicated that most of the shallow and deep-water samples show the distribution of a mixture of cations, while the produced water is biased towards the type of Na+K.

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