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Groundwater geochemistry and environmental isotopes of the Hodna area, Southeastern Algeria

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ABSTRACT

The intensive exploitation of groundwater resources in the region of Hodna (Southeastern Algeria) has greatly influenced the hydrochemical functioning of the shallow aquifer. This resulted in a significant decline in the piezometric level of the aquifer. In terms of hydrochemical facies, water is Ca-HCO_3 type in the Northern part of the plain due to limestone formations and SO_4-Cl-Na type in the South, because of the closeness of a salt lake. Eighteen groundwater samples were sampled and analyzed, in order to highlight the groundwater hydrochemical processes. Multivariate statistical techniques were applied to the obtained analyses on groundwater quality, with the purpose of defining the main controlling factors affecting the Hodna plain hydrochemistry. The statistical analysis reveals the presence of three groups, presenting an increased potential of salt proportionally to groundwater flow direction. Initially, in the aquifer boundaries and in the infiltration areas the facies result as bicarbonate. In the southern part of the plain, groundwater becomes SO_4-Cl rich, because of the dissolution of salt formations and the presence of the Hodna salt lake. Nitrate concentrations could be related to agricultural activities in the plain. Isotopic analyzes showed that the aquifer recharge is very quick and its groundwater have undergone high evaporation at the salt lake.

Keywords: Algeria; Hodna; Aquifer; Hydrochemistry; Isotopes; Multivariate statistical

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1. Introduction

Groundwater is an essential and vital resource worldwide. It was estimated that approximately one-third of the world's population uses groundwater for drinking [1–2]. The Hodna region, in the Algerian arid zone, is marked by a large open depression of 8500 km^2 surrounded by mountains, with the "Chott El Hodna" (salt lake, in local language) (1100 km^2) salt Lake in the Middle. This morphology allowed the installation of a low endorheic hydrographic network that supplies the salt lake by surface water especially during random heavy thunderstorms. The Chott is undergoing an excessive groundwater and surface water evaporation. In this area, where irrigated agriculture was developed over the last 50 years, two aquifers, shallow

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and deeper, exist [3]. Water level in the shallow aquifer strongly decreases because of the excessive withdrawals [4], and thus it presents significantly high salt concentration. On the other hand, the deeper aquifer with low salt concentration is the only source of water in the plain [5]. Its recharge appears to be easy due to the large extension of its hydrogeological watershed. However, the piezometric level is progressively lowering by the over-exploitation by uncontrolled pumping [6]. This excessive withdrawal generates a progressive degradation of the water quality in the irrigated area with the occurrence of high salinity zones (EC > 3500 μS/cm) and high contamination by nitrate, which harms the groundwater quality [7]. Dissolution, precipitation and ion exchange constitute the hydrochemical processes occurring within this system. These phenomena occur along the groundwater flow and they also depend on the residence time, which controls the evolution of groundwater chemical composition [8]. The dissolution of minerals of aquifer rocks is the main factor controlling the chemistry of these waters. Indeed, some minerals such as carbonates and evaporites dissolve rapidly and influence significantly the chemistry of the water, while others such as silicates dissolve more slowly and therefore have less effect on water chemical composition [9]. Several statistical techniques have been applied to study, assess and characterize the chemical changes in groundwater such as Factor analysis (FA) and cluster analysis (CA) [10]. Utilized FA to study the geochemical evolution, mineralization and groundwater contamination. Additionally, the CA method was used to interpret the hydrochemical data based on factor scores [11], and to study the chemical evolution of water along groundwater flow [12,13].

For thermodynamic equilibrium, the tendency of chemical equilibrium between the dissolved and the solid phases has been approached by means of the saturation index, which expresses the degree of chemical equilibrium between water and the solid matrix in the aquifer and it can be considered as a measure of the dissolution and/or precipitation in the study of water-rock interaction [9–14]. The use of PHREEQC code allows calculating the saturation indices of some carbonate and evaporite minerals [15].

This investigation concerns deep aquifers situated along the shoreline of Hodna Chott, which is the main endorheic lake in the region. The main objectives of the present work are: (1) characterizing the chemistry of groundwater; (2) determining the origin of the present chemical elements; (3) identifying the groundwater contamination processes; (4) highlighting the main factors of degradation of the water quality of this ecosystem; (5) reconstructing of the origin and recharge mechanisms of the aquifer by using geochemistry, environmental isotopes and multivariate statistical techniques.

2. Materials and methods

2.1. Study area

The investigated area is located in the South-East of Algeria, between Djebel Maadid (1863 m) to the North and Hodna Chott (450 m) to the South. The topography is a nearly flat plain, with a slope not exceeding 2% and, the highest altitude is 455 m. The region is characterized by annual rainfall, temperature and evapotranspiration of 215 mm, 19°C and 1700 mm respectively. In the summer, temperatures rise up to 50°C [16]. This area is characterized by an extreme spatio-temporal variability of rain [17]. During the last decade, this dryness condition accentuates the drawdown of water resource, especially because the water renewal has been very weak [16]. The dry climate, the atmospheric dust and the low intensity of precipitation affect the groundwater quality, generally causing an increasing of salt content [16].

The study area hosts more than 150,000 inhabitants, distributed across the plain. Agriculture remains the main activity as well as growing of market vegetables and cereals (barley and corn). Agriculture is developed where water resources are accessible, i.e. in the sandy area at south of the Chott El Hodna. According to [5], the arable land area is 50,000 ha, 50% of which is irrigated. Conventional farming requires the use of fertilizers such as ammonium nitrate, urea, phosphorus and potassium, superphosphate, potassium chloride and to a lesser extent, ammonium sulfate, sodium nitrate, calcium and potassium sulfate [16]. The absence of a wastewater treatment plant induces the discharge of liquid wastes in the nature, flowing into the groundwater by simple infiltration. Leaching of fertilizers used excessively and without any control harms the groundwater quality in the study area.

2.2. Geological and hydrogeological setting

The geological map of the area [18] shows the following main units: (1) Jurassic carbonate, (2) Cretaceous carbonate, (3) Mio-Pliocene clay and gypsum sand, (4) Quaternary alluvium formations (Fig. 1). Jurassic and Cretaceous carbonate rocks are dolomitic limestone and sandstone, sometimes with thick marl layers, about 550 m thick. The Mio-plio-quaternary unit is represented by heterogeneous continental detrital deposits, corresponding to red clay, sometimes gypsum overlaid by lacustrine limestones, conglomerates and alluvium. The thickness of this formation varies between 300 and 500 m.

The study concerns the deep aquifer of the Mio-Plio-Quaternary alluvial plain. Deep groundwater water table mainly occurs at 10 m in Southern and at 100 m in northern below the surface. The substratum of the shallow groundwater bearing unit is formed by Mio-Pliocene clays and marls, locally with gypsum deposits. Pumping tests on different wells showed that the transmissivity ranges between 10^{-5} in Southern and 10^{-2} m^2 s^{-1} in northern [16]. The aquifer is recharged by infiltration of meteoric water in the basin and by stream water coming from North ridges surrounding the plain. This region undergoes heavy pressures both natural such as climate aridity and anthropic such as overexploitation of water resources, and also agriculture activities [7]. Since several decades, important changes in land use and exploitation of water resources have occurred, induced by successive agricultural policies in Algeria, the agricultural revolution, the access to private land property and the national program of agricultural development [5]. Piezometric investigations performed during the dry period of 2012 showed a high piezometric level in the North, which decreased regularly towards the South, emphasizing the importance of hills for the groundwater recharge. Globally,

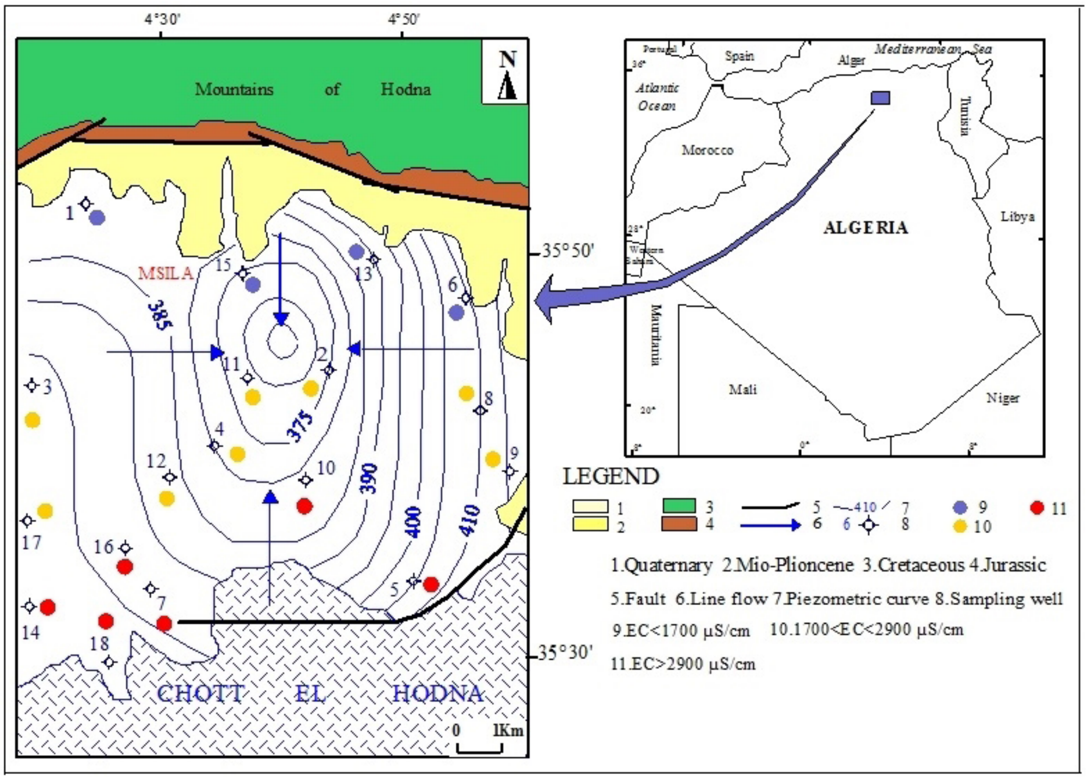

Fig. 1. Situation of study area sampling wells.

the groundwater flow directions are converging towards the center of the plain (Fig. 1). This condition of groundwater suggests a recharge coming from the cretaceous limestone in the North, while in the South by salt lake, finally a discharge in the center caused by exploitation wells. This situation generated an imbalance in the hydrogeological system and induced a reversal of flow, as observed in other parts of the region [19].

2.3. Sampling and analysis

To investigate the evolution of the physico-chemical parameters, 18 samples were taken during September 2012. Samples were collected after a pumping time of 15 min for stabilization of water temperature, by using two polypropylene bottles washed with acid. Each sample was immediately filtered in situ through 0.45 µm filters of acetate cellulose. Filtrate aliquots for cations analyses were transferred into 100 cm^3 polyethylene bottles and immediately acidified to pH < 2 by the addition of Merck™ ultrapure nitric acid (5 ml 6 N HNO_3). Samples for anions analyses were collected into 250 cm^3 polyethylene bottles without acidification. All samples were stored in an ice chest at a temperature <4°C and later transferred for analyses in the laboratory of the National Agency of Water Resources of Constantine. Immediately after sampling, pH, Temperature (T_w), electrical conductivity (EC) parameters were measured in the field by utilizing a multi-parameter WTW (P3 MultiLine pH/LF-SET). The following chemical elements have been analyzed: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), chloride (Cl^-), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), and nitrate (NO_3^-). The samples were analyzed according to the methods of the American Public Health Association [20]. The accuracy of the chemical analysis was verified by calculating the ion balance, the errors were generally within 5% (Table 1). The stable isotope analyses were performed in the Laboratory of Isotopes Hydrology in Turin (Italy) by using a Finnigan-Matt 251 mass spectrometer. For hydrogen, samples were reacted at 750°C with Cr metal using a Finnigan H/device coupled to the mass spectrometer. Oxygen, samples were equilibrated with CO_2 gas at approximately 15°C in an automated equilibration device coupled to the mass spectrometer and analyzed using continuous flow [21]. Standardization is based on the international reference materials VSMOW (Vienna Standard Mean Ocean Water).

2.4. Multivariate statistical

FA is often applied in the treatment of chemical data. Although FA is an exploratory and descriptive method, it is used also to identify the main factors that control the chemistry of the groundwater [22]. The multivariate statistical method has been widely applied to determine the phenomena of the environment around the world [23,24] and was used successfully to study the hydrogeochemical processes [25] and to estimate the degree of mutually shared variability between individual pairs of water quality variables. This kind of study is very helpful tool in promoting research and opening new frontiers of knowledge [26]. Kaiser [27] proposed to use only the factors with eigenvalues exceeding 1. Under this criterion, only factors with eigenvalues greater

Table 1
Statistical summary of hydrochemical parameters of groundwater. All values are in mg/l, except pH, EC in µS/cm, ^{18}O and ^{2}H

Wells	pH	EC	TDS	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}	NO_3^{-}	$\delta^{18}O$	$\delta^{2}H$
1	7.71	1653	1340	269	99	50	5	401	277	544	26	–6.6	–48
2	7.62	2150	1650	99	68	46	2	750	286	345	10	–6.3	–43
3	7.25	2350	1860	222	124	191	1	228	849	233	22	–6.7	–43
4	7.15	2140	1650	247	86	106	2	220	658	349	28	–5.2	–44
5	7.01	3280	2230	452	228	554	2	309	1207	288	10	–7.2	–45
6	7.45	1210	930	421	111	115	8	205	360	665	9	–5.4	–52
7	7.36	3005	2330	100	81	554	1	516	920	294	4	–8.8	–58
8	7.46	2300	1770	186	101	215	3	108	1032	254	6	–6.0	–56
9	7.59	2653	2130	184	110	340	3	678	533	210	20	–6.3	–57
10	7.62	2900	2560	177	139	400	3	835	743	260	1	–8.7	–56
11	8.22	2200	1880	128	117	348	1	344	930	342	1	–6.4	–57
12	7.12	2380	1940	200	168	325	6	476	1025	228	15	–6.5	–55
13	7.85	1025	810	220	82	59	2	234	350	666	33	–6.5	–55
14	7.48	3210	2620	149	146	420	5	845	733	251	1	–8.2	–53
15	7.46	1554	1230	307	133	90	1	163	248	668	2	–5.7	–49
16	8.23	3300	2470	119	138	318	1	344	918	346	5	–9.0	–59
17	7.40	2827	2040	100	105	82	1	102	345	325	1	–9.4	–62
18	7.42	3088	2670	99	107	507	2	518	925	288	4	–8.7	–55
Min	7.01	1025	810	99	68	46	1	102	248	210	1	–9.4	–62
Mean	7.50	2401.4	1895	204.4	119.1	235.7	2.7	404.2	696.6	358.4	11.0	–7.1	–52.8
Max	8.23	3300	2670	452	228	554	8.0	845	1207	668	33	–5.2	–43
SD	0.30	680.7	541.3	101.9	36.3	163.2	2.0	234.8	293.4	143.0	10.2	1.4	5.9
Skew	0.80	–0.5	–0.50	1.20	1.50	0.50	0.4	0.80	–0.20	1.3	0.9	–0.5	0.5
AHG^{f}	6.5–9	2800	1500	200	/	200	12	500	400	/	50	/	/

Min: minimum value; Mean: average value; Max: maximum value; SD: standard deviation; Skew: skewness; AHG: Algerian health guidelines

or equal to 1 will be accepted as possible sources of the variance in data, ascribing the highest priority to the factor with the highest eigenvector sum. The reason for choosing the threshold 1 is that a factor in order to be acceptable must have a variance as large as that of a single standardized original variable [28].

CA is also another data reduction method, used to classify entities with similar properties. There are two types of CA: R and Q-modes. The advantage in using the hierarchical method of CA applied is because it does not require any prior knowledge of the number of cluster [10]. CA comprises a series of multivariate methods which are used to find true groups of data [10]. In the present work, CA was applied using the Euclidian distance as a measure among the samples, and Ward's method as a linkage rule for the hydrogeochemical data classification in the Hodna area.

2.5. Thermodynamics

The thermodynamics was conducted using the PHREEQC code to calculate the saturation indices (SI) and the tackle speciation minerals. The SI was calculated according to Eq. (1).

$$SI = \log (IAP/K) \quad (1)$$

where IAP is the ion activity product of the mineral water reaction and K is the thermodynamic equilibrium constant. The SI minerals are used to evaluate the state of saturation of the water and to control its chemistry and equilibrium with the solid phase [9]. In general, the water-rock equilibrium is reached when SI = 0. If SI > 0, the water is supersaturated and, precipitation of minerals is necessary to obtain equilibrium, if SI < 0, water is under saturated, dissolution of minerals is necessary for reaching equilibrium [29].

All statistical computations were made using Excel 2010 (Microsoft Office®) and STATISTICA 6 (Stat Soft, Inc.®).

3. Results and discussion

3.1. General hydrochemistry

Descriptive statistics for each parameter were determined. Special attention was brought to the value of skewness, which is an indicator for the symmetry of a distribution. The results show that all distributions of the concentrations are positively skewed except for EC and TDS (Table 1). Skewness values are close to zero except for Carbonate elements (Ca^{2+}, Mg^{2+} and HCO_3^{-}), which are slightly higher. As a consequence, all parameters were assumed to follow a log-normal distribution [30] and each distribution has a zero mean and the values for each parameter are measured in standard deviation units [31].

Examination of the statistical characteristics of the chemical analyzes (Table 1) shows that the pH values range from 7.01 to 8.23, with a mean value of 7.5 (±0.3). These values are characteristic of a shallow aquifer in arid areas [16]. It is known that the processes of calcite and dolomite buffering are dominant for the pH range 6.5 to 7.5 [32]. Furthermore, lithological formations contain limestone, an environment where several redox reactions may occur, inducing dissolution of carbonates. In general, the groundwater is a little alkaline, but the quality lies within the limiting value of the drinking water standard. The general increasing of pH in a sedimentary terrain is related to weathering of plagioclase feldspar in sediments. This is aided by dissolved atmospheric carbon dioxide, resulting in the releasing of sodium and calcium, which progressively increases pH and alkalinity of the groundwater. For the 18 groundwater samples analyzed, 61% of pH measures are found in this range.

Salinity, represented by the EC (Fig. 1), increases from the center of the plain to the salt lake; it passes from 1025 µS/cm to 3300 µS/cm. This is the result of the inversion of the flow from the salt lake towards the plain, due to the drawdown induced by pumping. This phenomenon has been noticed in other parts of the country, as highlighted by several authors [33–35]. Low values (EC < 1700 µS/cm) were recorded for water samples along the northern piedmont and constitute 22% of cases. They correspond to the recharge zone, as illustrated by the piezometric map. The second group of samples shows a salinity varying between 1700 and 2900 µS/cm and constitutes 45% of cases. It characterizes some samples collected from the center plain. The third group has a salinity values greater than this limit and constitutes 33% of cases. They are concentrated near the salt lake. The main reasons are the intrusion of residual solids into the aquifer, and the movement of water through sediments containing higher soluble mineral matter.

Alkalinity varies from 210 mg/l to 668 mg/l, with a mean value of 358.4 ± 143 mg/l. Na$^+$ varies from a minimum of 46 mg/l to a maximum of 554 mg/l, with a mean value of 235.7 ± 163.2 mg/l. K$^+$ ranges from 1 mg/l to 8 mg/l, with a mean value of 2.7 ± 2 mg/l. Ca^{2+} ranges also from 99 mg/l to 452 mg/l, with a mean value of 204.4 ± 101.9 mg/l. Mg^{2+} varies from 68 mg/l to 228 mg/l, with the mean value of 119.1 ± 36.3 mg/l. Cl$^-$ varies from 75 mg/l to 845 mg/l, with a mean value of 366.7 ± 230.4 mg/l. SO$_4^{2+}$ ranges from 248 mg/l to 1207 mg/l, with a mean value of 696.6 ± 293.4 mg/l. NO$_3^-$ varies from 1 to 33 mg/l, with the mean value of 11 ± 10.2 mg/l. Higher mean values of Na$^+$, Cl$^-$, and SO$_4^{2+}$ indicate a likely contamination by high salinity waters of the lake and a dissolution of evaporate minerals.

The abundance of the major anions is SO$_4^{2-}$ > Cl$^-$ > HCO$_3^-$, 73% of samples exceeded the maximum acceptable concentration of SO$_4^{2-}$ for drinking water (200 mg/l), and 28% of samples overcame the maximum acceptable concentration of Cl$^-$ for drinking water (500 mg/l). The abundance of the major cations is Na$^+$ > Ca^{2+} > Mg^{2+} > K$^+$ and 50% of samples exceeded the maximum acceptable concentration of Na$^+$ for drinking water (200 mg/l), whilst 45% of samples showed values of Ca^{2+} higher than the maximum acceptable concentration for drinking water (200 mg/l) [2]. Groundwater samples were plotted in a (Cl$^-$ vs Ca^{2+} + Mg^{2+}) diagram [36] to show the different water types in the study area (Fig. 2). This diagram shows that the overall chemical character falls within the following water types:

- Fresh groundwater with low salinity concentrations, located in the northern part of study area;
- Saline water with high salinity concentrations, located in the southern part.

These salt waters, located in the nearby of the Hodna lake, reflect the impact of saline water intrusion and associated processes (halite and gypsum dissolution and/or pyrite oxidation), and anthropogenic pollution at well head.

NO$_3^-$ values varied from 1 to 33 mg/l, with the mean value of 11 ± 10.2 mg/l. The low concentration of nitrate is probably due to both the agricultural activity, and the high salinity of water and soil.

3.2. Water types

The different water samples have been classified according to their chemical composition using the Piper diagram (Fig. 3). This diagram consists of two triangular and/or one intervening diamond-shaped fields. The percentage reacting values at the three cation groups Ca^{2+}, Mg^{2+}, and (Na$^+$ + K$^+$) are plotted as a single point in the left triangular field, then the three anion groups (HCO$_3^-$ + CO$_3^{2-}$), SO$_4^{2-}$, and (Cl$^-$ + NO$_3^-$) similarly on the right triangular field. Basically, water type was determined from a combination of the principal cation and anion based on concentrations expressed in percentage of meq/l. Using this method, three water types (facies) were defined for the study area. The analysis showed that calcium–bicarbonate (Ca^{2+}–HCO$_3^-$) water type characterized 22% of samples, mainly located in the north of the study area. The presence of fractured and karstified limestone formations on the north boundary suggest an infiltration of rain water where they acquire a calcite facies, which explains the presence of low salinity water (EC < 1700 µS/cm) on the north part. SO$_4^{2-}$-Cl$^-$ -Na$^+$ water type characterizes 33% of all the samples collected, this condition is mainly detected along the salt lake, in the southern part of the study area. This explains the presence of high salinity (EC > 2900 µS/cm) water in that portion of the study area. This facies is related to salty formations around the salt lake such as marl and clays. The remaining water samples (45%) are intermediate water types between those previously mentioned, they are sulfate-dominant types (SO$_4^{2-}$-HCO$_3^-$-Ca^{2+}, SO$_4^{2-}$-Ca^{2+}-Mg^{2+}, SO$_4^{2-}$-Ca^{2+}, SO$_4^{2-}$-

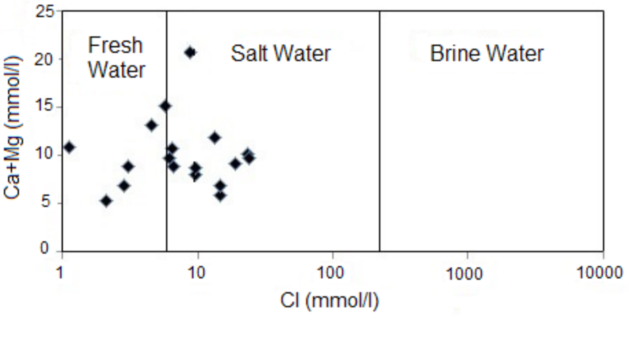

Fig. 2. Cl versus Ca and Mg in mmol/l for groundwater samples.

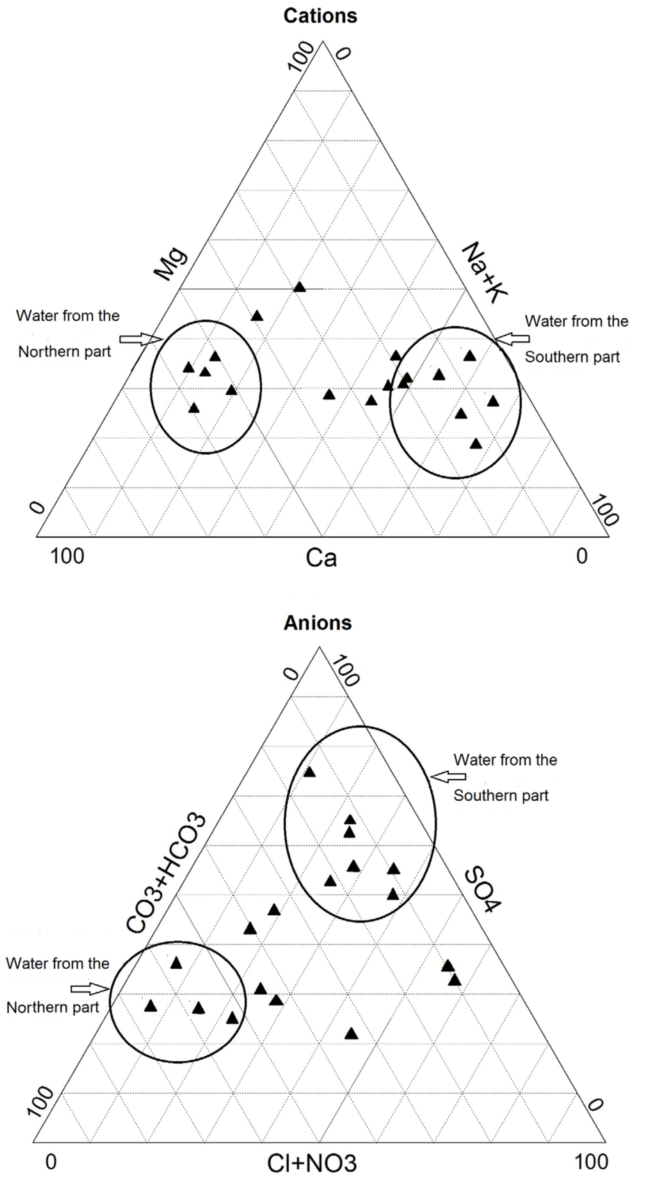

Fig. 3. Diagram Piper applied to water samples of Hodna aquifer.

Table 2
Variance explained and component matrixes

	F1	F2	F3
EC	0.78	0.43	0.39
Mg^{2+}	0.32	–0.69	0.49
Ca^{2+}	0.06	–0.56	0.09
Na^{+}	0.75	0.43	0.43
K^{+}	–0.32	–0.33	–0.49
$Cl^{–}$	0.66	–0.38	0.04
$SO_4^{2–}$	0.69	–0.62	–0.19
$HCO_3^{–}$	–0.05	–0.55	0.07
$NO_3^{–}$	–0.08	0.18	–0.68
Eigenvalue	2.98	2.02	1.59
Variance (%)	53	22	7
Cumulative (%)	53	75	82

The bold values indicate the correlated variables

Na^+-Ca^{2+}, and $SO_4^{2–}$-$Cl^–$). The electrical conductivity for this group ranges between 1700 to 2900 µS/cm, which is the characteristic of mixed water. So, the Ca^{2+}-$HCO_3^–$ water type represents replenishment and recharge from the recent meteoric water, while the $SO_4^{2–}$-$Cl^–$-Na^+ water type indicates leaching of the aquifer matrix of salt deposits.

3.3. Statistical analysis

3.3.1. Factor analysis

The FA was performed on 18 individuals and 9 variables (EC, Ca^{2+}, Mg^{2+}, Na^+, K^+, $Cl^–$, $SO_4^{2–}$, $HCO_3^–$ and $NO_3^–$). Table 2 shows the eigenvalues of the extracted factors and the proportion of the total sample variance explained by the factors. The analysis generates 10 factors, but only three factors were retained, which account for 82% of total variance. The parameter's weights for the three factors of the dataset are given in Table 2. The factor loading is classified as "strong", "moderate" and "weak", corresponding to absolute loading values of 0.75, 0.75–0.50, and 0.5, respectively [37]. Dalton and Upschurch [38] has shown that factor scores can be related to the intensity of a particular described process. Extreme negative values (close to –1) indicate areas essentially unaffected by the process and the positives scores (close to +1) are the areas of most affected.

EC, Na^+, $Cl^–$ and $SO_4^{2–}$ marked factor 1, which explained 53% of the variance, it has a strong to moderate positive loading in EC, Na^+, $Cl^–$ and $SO_4^{2–}$, which are 0.78, 0.75, 0.66, and 0.69 respectively. High positive loadings indicated strong linear correlation between the factor and the parameters. Thus, factor 1 (F1) can be considered as a salinization factor. Simultaneous drought and over pumping have led to deterioration of the groundwater quality. These variables indicate that the factor is the influence of the aquifer with different rock types. Groundwater aquifer, which consists of evaporite host rocks, can reach high concentrations of $Cl^–$ and $SO_4^{2–}$.

Factor 2 (F2) explains 22% of the total variance and has a moderate negative loading in Mg^{2+}, Ca^{2+} and $HCO_3^–$, which are –0.69, –0.56 and –0.55 respectively. These variables indicate that the factor is the influence of aquifer with carbonate rock types.

Factor 3 explains 7% of the total variance of the dataset, it shows a significant characteristic with K, Cl, and NO_3. It has strong negative loadings on $NO_3^–$ (–0.68) and weak loading on K^+ (–0.49) and $Cl^–$ (0.766). Factor 3 is mostly associated with evaporite host rocks and chemical fertilizers. Large amounts of fertilizer, such as urea and commercial compounds, have been applied for long time. Under oxidation conditions, NH, the main component of fertilizers, is easily oxidized to $NO_3^–$ by the nitrification process [39].

Table 3 shows the connection Factors-water samples. F1 shows an opposition between samples of the northern part (1, 15, 13 and 6) rich in $HCO_3^–$ with low salinity, and samples from the southern part (14, 18, 16, 7, and 10) rich in Na^+,

Cl^- and SO_4^{2-} with high salinity. On the other hand, F2 is determined by the samples in the center of the plain (17, 12, 2 and 5), characterized by an intermediate salinity with the exception of sample 5.

Through the same approach as for the parameters, the scores for each water sample were also calculated during the FA procedure. These scores represent the influence of the factor on the samples. Most samples from North boundary have positive scores on the first factors, indicating that they are characterized by low salinity content, and for Ca^{2+}-HCO_3^- water types. Most samples from South part of aquifer have returned negative scores on the second group of factors, indicating that they are characterized by high salinity content, and for SO_4^{2-}-Cl^--Na^+ water types.

Table 3
Factor loading for water samples

	F1	F2	F3
1	0.833	0.008	0.105
2	0.097	0.636	0.162
3	0.000	0.000	0.421
4	0.397	0.017	0.108
5	0.271	0.611	0.062
6	0.540	0.248	0.085
7	0.506	0.228	0.008
8	0.023	0.000	0.250
9	0.090	0.085	0.304
10	0.588	0.003	0.283
11	0.246	0.097	0.227
12	0.162	0.327	0.144
13	0.830	0.012	0.014
14	0.510	0.002	0.443
15	0.480	0.021	0.092
16	0.567	0.034	0.205
17	0.015	0.505	0.194
18	0.743	0.114	0.000

3.3.2. Cluster analysis

Two different methods can be applied to identify clusters, including R or Q-modes [38]. R-mode is usually applied to water quality variables to reveal their interactions, while Q-mode indicates the interactions between the studied samples. Eight hydrochemical measured variables (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-, and NO_3^-) were utilized in this analysis. For statistical purpose, all the variables were log-transformed in order to handle quasi-normally distributed data. Subsequently, they were standardized to their standard scores (*z*-scores) as described by [12]. Since there is no test to determine the optimum number of groups in the dataset [12], the visual inspection was the only criteria to select the groups in the dendrogram (Fig. 4). The defined phenon line [40] was chosen at a linkage distance of 18 for R-mode and 8 for Q-mode. At this distance, the groups could be distinguished in terms of their hydrochemical variables. As shown in Fig. 4, eight variables were classified into three groups of groundwater: the first group of variables (G1) formed by Ca^{2+}, Mag^{2+} and HCO_3^-; the second one (G2) involves principally Cl^- and SO_4^{2-} ions. The remaining variables, Na^+, K^+ and NO_3^- pH constituted the third group (G3) (Fig. 4).

These links can be interpreted together with the evolution trends defined in the basic hydrochemical study. The concentrations of Ca^{2+}, Mag^{2+} and HCO_3^- can be considered as the variables describing the process of carbonates dissolution occurring in the boundary areas during the recharge of the aquifer. On the other hand, the variables Cl^- and SO_4^{2-} can be identified as representative of other alternative salinization of the groundwater of Hodna aquifer, as the variables describing the process of the salt water intrusion from the Hodna Lake. Thus, Na^+, K^+ and NO_3^-, resulting from solute return flow from the development of irrigation, can be considered, also, as an imposed salinization mechanism. These variables would be found in natural

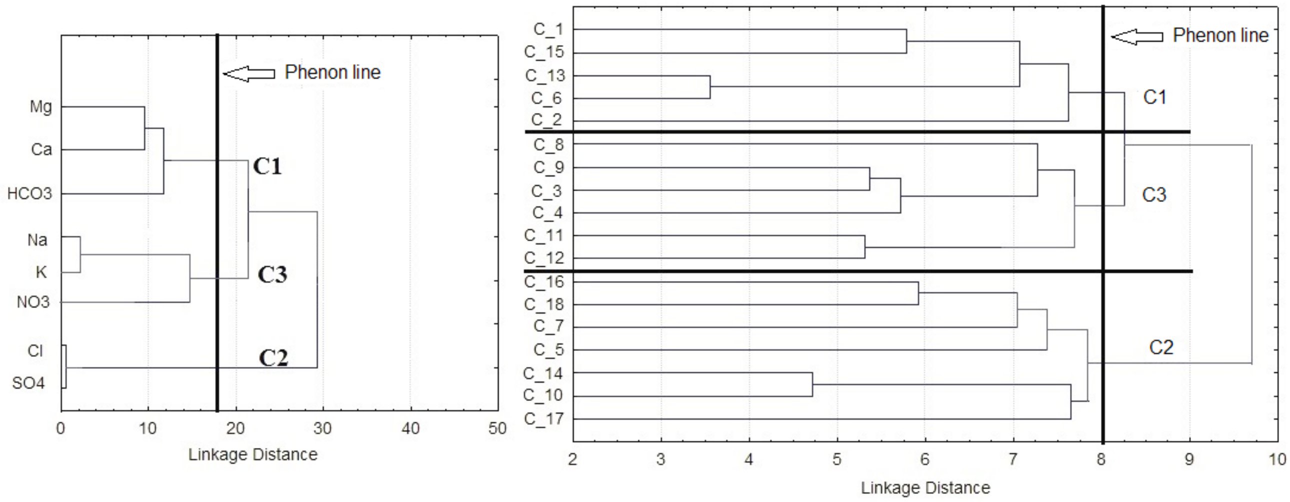

Fig. 4. Dendrogram of cluster analysis of variables and the hydrochemical samples.

mineralization and anthropogenic processes. The non-homogenous nature of the aquifer led to different hydrogeochemical facies for ground water such as Ca^{2+}-HCO_3^- in the northern fringe and SO_4^{2-}-Cl^--Na^+ in the south plain.

The G1 has a low salinity (EC < 1700 µS/cm), while G2 shows high salinity (EC > 2900 µS/cm), and G3 both intermediate and average salinity (1700 < EC < 2900 µS/cm). These groups of the samples; they are located in different areas. The G1 is located in the north, near the recharge zone, the G2 in the south, near the salt lake and the G3, in the center of the plain (Fig. 1). The G1 is composed by of well 1, 2, 6, 13 and 15, and it is characterized by Ca^{2+} and HCO_3^-. It is located to the north of the outcrops. G2 is found mainly along the salt lake in the south of the study area. This group is composed of the wells 5, 7, 10, 14, 16, 17 and 18. It is influenced by the Triassic saliferous formations as well as by the return flow from the salt lake and it is characterized by SO_4^{2-}-Cl^-. G3 is a term of transition between the two extremes groups and it is drawn from wells 3, 4, 8, 9, 11 and 12 and it is characterized by Na^+, K^+ and NO_3^- from the agricultural activity.

3.4. Water–rock interaction process

The calculation of saturation indices of the mineral phases gives an indication of the interaction between the groundwater and the aquifer rocks [41]. Based on this principle, the saturation indices (SI) of some evaporite minerals (gypsum, anhydrite and halite), carbonate minerals (calcite, aragonite and dolomite), and the partial pressure of carbonic gas (pCO_2) were calculated by means of PHREEQC code [15]. Table 4 shows the distribution of the computed pCO_2 values (on a log scale) for all the considered groundwater. It is known that the atmospheric pCO_2 is about $10^{-3.5}$ atm [42]. These computed values vary between $10^{-2.78}$ and $10^{-1.65}$ atm., so they are significantly higher than the atmosphere's one. Such elevated values suggest that the groundwater system is open to soil CO_2 [42].

Saturation indices show that the solution is undersaturated (–7.07 to –0.33) for the main evaporite minerals, reflecting a relatively long contact time with these minerals to allow dissolution, but saturated (–0.01 to 2.55) with respect to carbonate minerals. This is also in association with the equilibrium constant (K) of the evaporite minerals (NaCl (1.58) $CaSO_4$, $2H_2O$ (–4.58)), which are higher and that allows them to stay in water at high concentrations.

The Gibbs diagram is widely used to establish the relationship between water composition and aquifer lithological characteristics [14]. The Gibbs ratios are calculated by the formulae 2 and 3 given below:

$$\text{Gibbs Ratio I (for Anion)} = Cl^-/(Cl^- + HCO_3^-) \tag{2}$$

$$\text{Gibbs Ratio II (for Cation)} = Na^+/(Na^+ + Ca^{2+}) \tag{3}$$

where all ions concentrations are expressed in mmol/l.

The different water samples have been classified according to their chemical composition using Gibbs diagram (Fig. 5). The predominant samples (72%) fall into mixing and few (28%) samples into fresh water. Gibbs ratio I values in the present study varies from 0.11 to 0.85, with an average value of 0.56, while Gibbs ratio II values varies from 0.24 to 0.91, with an average value of 0.63. The first water type changed continuously due to both the influence of the water–rock interaction of the aquifer material that is mainly composed by evaporite facies, and the influences

Table 4
Saturation indices of some minerals

	Aragonite	Calcite	Dolomite	Log pCO_2	Anhydrite	Gypsum	Halite
Samples	$CaCO_3$	$CaCO_3$	$CaMg(CO_3)_2$		$CaSO_4$	$CaSO_4 \cdot 2H_2O$	NaCl
1	1.04	1.18	2.28	–2.05	–1.17	–0.95	–6.34
2	0.39	0.54	1.25	–2.12	–1.43	–1.21	–7.07
3	0.07	0.21	0.50	–1.95	–0.83	–0.61	–6.02
4	0.22	0.36	0.61	–1.67	–0.85	–0.63	–6.28
5	0.14	0.29	0.62	–1.65	–0.55	–0.33	–5.46
6	1.02	1.17	2.11	–1.71	–0.95	–0.73	–6.28
7	–0.10	0.04	0.33	–1.95	–1.14	–0.92	–5.21
8	0.21	0.36	0.78	–2.12	–0.82	–0.60	–6.29
9	0.30	0.45	1.01	–2.34	–1.09	–0.87	–5.30
10	0.36	0.51	1.26	–2.28	–1.02	–0.80	–5.15
11	0.91	1.05	2.40	–2.77	–1.04	–0.82	–5.58
12	–0.16	–0.01	0.24	–1.83	–0.85	–0.63	–5.48
13	1.17	1.31	2.55	–2.10	–1.13	–0.91	–6.50
14	0.14	0.28	0.90	–2.15	–1.09	–0.87	–5.12
15	0.93	1.07	2.13	–1.71	–1.20	–0.98	–6.48
16	0.89	1.04	2.47	–2.78	–1.08	–0.86	–5.62
17	0.13	0.27	0.91	–1.94	–1.40	–1.18	–6.70
18	–0.05	0.09	0.55	–2.02	–1.15	–0.93	–5.25

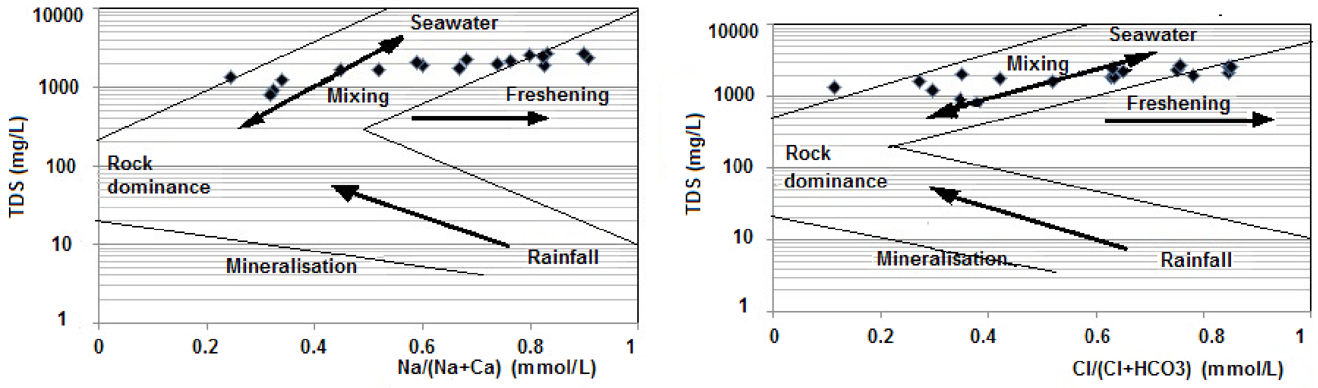

Fig. 5. Gibbs diagrams for water samples of the Hodna aquifer.

of human activities, and finally the irrigation return flow. The result is indicated by a rapid increasing in sodium, sulfate and chloride concentrations in the groundwater. The second water type is influenced by carbonate rock at the northern boundary.

The controls of the hydrochemical evolution of groundwater largely depend on the chemistry of the recharging water, water aquifer matrix interaction, or both, as well as groundwater residence time within the aquifer. Two general processes contribute to the generation of solutes in groundwater: evaporate dissolution and carbonate dissolution [43]. The chemistry of the evolving water depends not only on the bulk chemistry of the matrix, but also on the weathering rate [44]. Hence, even relatively minor proportions of carbonates and evaporates can significantly influence water chemistry [28]. For example, Ca^{2+} and Mg^{2+} originate from the weathering of carbonates, silicates and evaporites, Na^+ and K^+ from the weathering of evaporites and silicates, HCO_3^- from carbonates and silicates, SO_4^{2-} and Cl^- from evaporites [45]. To understand these hydrogeochemical processes, we utilized the ion correlation diagrams made in molar concentrations of the main major elements. The first diagram was affected by the variation of evaporate elements. The liaison Na^+ *vs* Cl^- shows that the majority of the water samples are aligned along a straight line having a slope of 0.71, slightly different from that one of the halite dissolution with a line of slope 1 (Fig. 6a). So, Na^+ and Cl^- are largely derived from the dissolution of halite [46], the geological environment is very rich in evaporite minerals. The second diagram $Ca^{2+} + Mg^{2+}$ vs $SO_4^{2-} + HCO_3^-$ can highlight the origin of Ca^{2+}, Mg^{2+} and SO_4^{2-}. If the analytical points fall around the straight line slope 1:1, the dominant reactions are due to the dissolution of calcite, dolomite and gypsum. Ion exchange tends to move the points either upwardly due to either excessive $Ca^{2+} + Mg^{2+}$, or downwards due to the excess $SO_4^{2-} + HCO_3^-$ [47]. It is therefore clear that the chemistry of the water in the region is generally influenced by the dissolution of calcite, dolomite and gypsum, and by ion exchange, or the salinity is due to the influence of the Hodna lake (Fig. 6b). This is confirmed by the third diagram Ca^{2+} vs SO_4^{2-} (Fig. 6c). The infiltration of the rain water through the carbonate formations in the northern part of study area allows the dissolution of limestones and dolomites of Cretaceous and Jurassic. During the groundwater flow, the water allows the dissolution of gypsum and/or anhydrite of the Mio-Plio-Quaternary age. The last diagram Ca^{2+}+Mg^{2+}+HCO_3^-/Na^++K^++Cl^-+SO_4^{2-} vs TDS can demonstrate the global origin of salinity (Fig. 6d). In fact, in this diagram two groups can be individualized by their salinity: samples with low salinity (TDS < 1700 mg/l) and dominated by carbonates coming from the northern part, and those with high salinity (TDS > 1700 mg/L) and dominated by salty minerals from the southern part.

3.5. Groundwater isotopes

The use of stable isotopes is crucial for evaluating of the origin and evolution of groundwater [48]. Isotopic methodologies are nowadays well established in hydrological studies of groundwater system [49]. Stable isotopes of oxygen and hydrogen in groundwater give the initial isotopic composition of recharging rainwater in hydrological cycle [48–50]. Within the coordinate system of $\delta^{18}O$ and δ^2H, we can provide information on precipitation, evaporated surface water and seawater sources, and thus can help to identify the origins of groundwater salinity [51]. The $\delta^{18}O$ and δ^2H values of the investigated groundwater samples are shown in Table 1. Stable isotopes of water points sampled in this study present a wide range of variation between –9.4 and –5.2 in $\delta^{18}O$ with a mean of –7.1 ± 1.3‰, and from –62.0 to –43.0 in δ^2H with a mean of –52.8 ± 5.8‰. In Fig. 7, measured values of $\delta^{18}O$ and δ^2H from the investigated groundwater samples are compared with the global meteoric water line (GMWL: $\delta^2H = 8\ \delta^{18}O + 10$), defined by [52]: the groundwater samples are distributed around a line intersecting the global meteoric water line, with a slope equal to $\delta^2H = 2.3\ \delta^{18}O -36.5$ (Fig. 7). The isotopic content of the aquifer in δ^2H and $\delta^{18}O$ reveals two practically equal water groups. The first group comprises water samples closely aligned with the GMWL and indicates no significant isotopic modifications by evaporation, which means that the recharge of the aquifer is quite rapid. This group is composed essentially of wells (1, 15, 13, 6 and 11) located to the north near the recharge zone and secondarily two wells (7 and

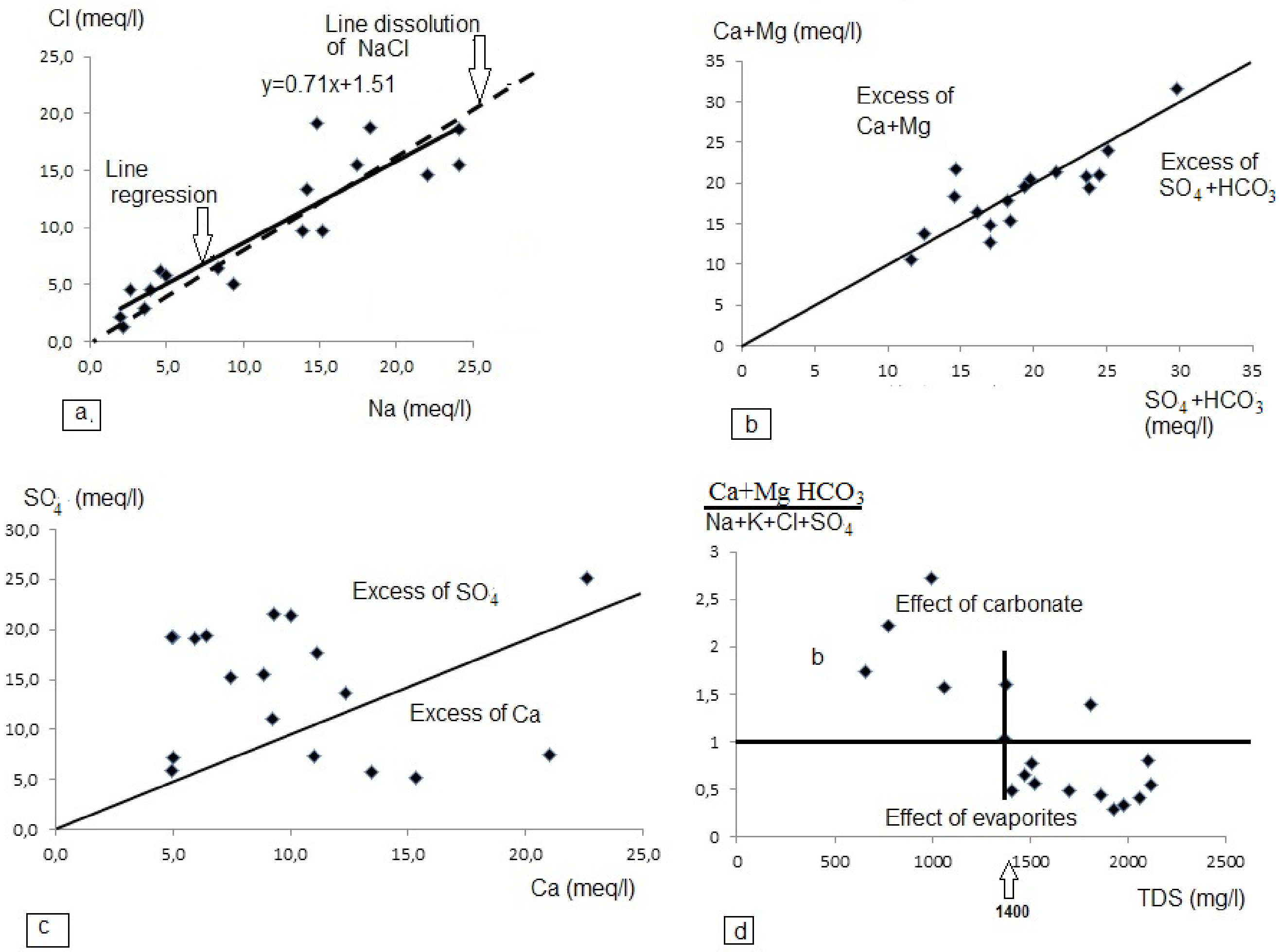

Fig. 6. Plot of (a) Na$^+$ *vs* Cl$^-$ (b) Ca^{2+}+Mg^{2+} *vs* SO$_4^{2-}$+HCO$_3^-$ (c) Ca^{2+} *vs* SO$_4^{2-}$ (d) TDS *vs* Ca^{2+}+Mg^{2+}+HCO$_3^-$/Na$^+$+K$^+$+Cl$^-$+SO$_4^{2-}$.

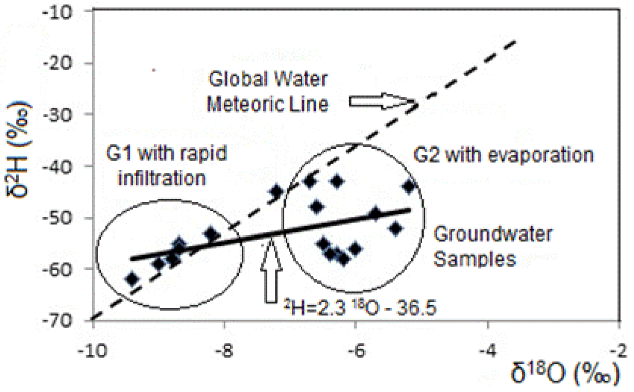

Fig. 7. δ^{2}H versus δ^{18}O relationship for groundwater in the Hodna area.

14) located to the south of the plain. The second group is closely below the meteoric water line, indicating that groundwater has been influenced by evaporation [53,54] and the salt waters of the Lake. This group is composed essentially of the wells located to the south of the plain in the discharge zone (Fig. 8).

4. Conclusion

A groundwater quality assessment of the Hodna area based on 18 groundwater samples showed that Ca–HCO$_3$ water type is found in the North of the study area, which characterizes waters with low mineralization, located in recharge areas at higher elevations. Other important water type is the SO$_4^{2-}$-Cl$^-$-Na$^+$ one, observed mainly along the salt lake in the south of the study area, which characterizes waters of high mineralization. These observations were supported by a multivariate statistical analysis, including FA and CA. The first factor of FA was related to salinity parameters (EC, Na$^+$, SO$_4^{2-}$ and HCO$_3^-$), the second one to the carbonate content (Mg^{2+} and Ca^{2+}), and the third one is mostly associated with evaporite host rocks (Cl$^-$) and chemical fertilizers content (K$^+$ and NO$_3^-$). Thus, FA gave a general idea of the processes involved in the chemical evolution of groundwater. Using CA, samples were classified into groups according to their similarity. The G1 with low salinity (EC < 1700 µS/cm), G2 with high salinity (EC > 2900 µS/cm) and G3 with intermediate and average salinity (1700 < EC < 2900 µS/cm). Only the waters of G1 and G3 can be exploited. On the other hand, the waters of G2 are not exploitable because of the high salinity, resulting from

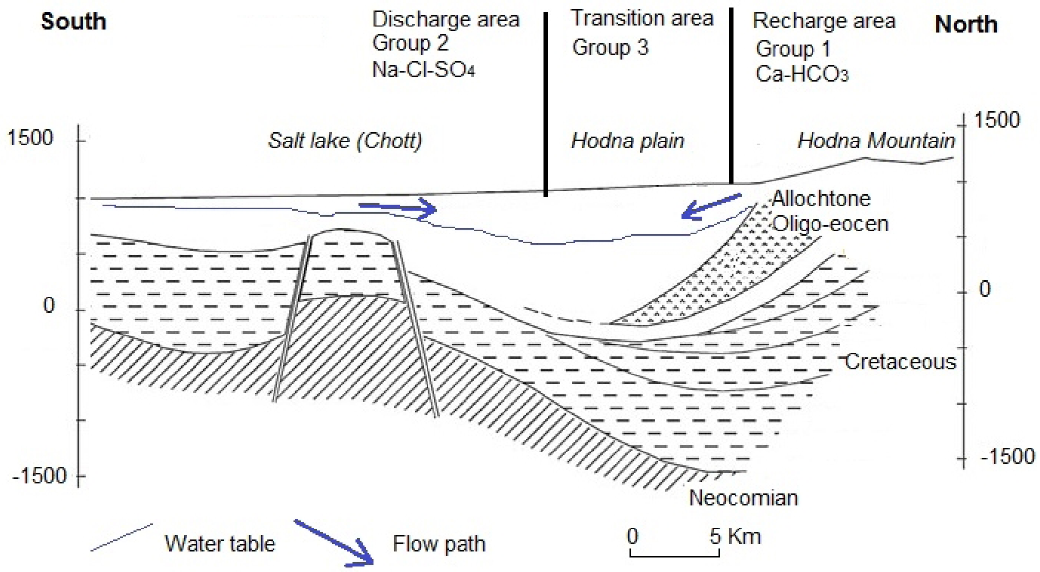

Fig. 8. Schematic section along the groundwater flow path.

the flow inversion coming from the Hodna salt lake to the center of the plain, while initially this lake was the main natural discharge area.

The isotopic content of the aquifer in δ^2H and δ^{18}O reveals two practically equal water groups. The first group indicates no significant isotopic modifications by evaporation, which means that the recharge of the aquifer is quite rapid by the Northern boundary. The second group indicates that groundwater has been influenced by evaporation and the salt waters of the Hodna lake in the discharge zone.

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