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Groundwater hydrochemistry and effects of anthropogenic pollution in Béchar city (SW Algeria)

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ABSTRACT

Béchar city is located in the southwest part of Algeria, characterized by an arid climate with Saharan tendency. It is subject to an increasing demand for water like all the great agglomerations, due to the economic and demographic development. In spite of a rate of rather significant connection with drinking water feeder system, the groundwater remains solicited for daily human activities (irrigation, sanitation, etc.). However, after use, the wastewater are rejected into Béchar wadi (river), which flows along the city, where the sewerage is discharged without treatment, causing a real threat to the environment, particularly to the groundwater, due to the nature and the hydrodynamic aquifer system in the city. The identification of facies, principal component analysis, Gibbs diagram, and reporting features have all given satisfactory results. This facies varies with dilution (wet period) or concentration (dry period) preferably elements of Cl^-, Ca^{2+}, SO_4^{2-}, Na^+, and HCO_3^-, depending on groundwater recharge. The chemistry of groundwater is related to a mechanism of acquisition that depends on the hydrogeology of the city and the significant anthropogenic input.

Keywords: Béchar; Wastewater; Groundwater; Hydrochemistry; Anthropogenic contributions

1. Introduction

Major cities in developing countries generally experience rapid population growth that generates multiple and complex problems [1–3]. On top of the challenges that pose high demand and water management, are added problems relating to its quality, and in our case to the influence of arid climate on water resources (availability) [4,5]. The groundwater pollution by domestic sewage in an urban environment is a problem that is growing in importance, and many scientists have studied it by several approaches, such as physicochemical, statistical and microbiological, and so as transfer mechanisms contaminants into this groundwater. Determining the origin of the chemical elements in groundwater can lead to the identification of the parameters of anthropogenic origin, as well as the understanding of the acquisition mechanisms of natural and/or anthropogenic chemistry in these waters [6,7]. In this paper, a triple objective is pursued: first of all, the spatiotemporal characterization of groundwater chemistry, and then the mechanisms of

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acquisition of chemical elements composing their mineralization, and in the end, the identification of anthropogenic inputs in these waters.

2. Materials and methods

2.1. Study area

The city of Béchar is located in the southwest of Algeria (Fig. 1), with an arid climate to Saharian tendency. Rainfall is erratic during the year, with an average of about 72 mm for the period of 1988–2008. The lowest temperature (4°C) was recorded in January and the highest (40°C) in July, with an average of 27.16°C. The average evaporation is 306 mm, while the values of evapotranspiration exceed those of rainfall, involving a drought throughout the year [8]. Béchar is like all Algerian cities, which have a high water demand proportional to the increase in the population, with a growth rate of 3.11% (in 2007 the population was 161,902 inhabitants) [8]. The city of Béchar extends over an area of approximately 160 km. It is connected to the main drinking water at a rate of 99%, with an actual staffing estimated at 139 liters/capita/day and a satisfaction rate of 71%. However, groundwaters are widely used for irrigation, Turkish baths, public showers, mosque, etc. [8]. The wadi crosses on its path, from north to south, the former Quaternary alluviums of variable thickness between 5 and 10 m, the Eocene limestones said Barga II, thicker than 60 m, then the limestone Turonian said Barga I with a thickness ranging from 25 to 45 m of interbedded limestones and sandstones of the Carboniferous Westphalian and finally a lateral contact with the alluvium adjacent Namurian [9–12].

2.2. Methodology

The physicochemical composition of water plays an important role in determining its quality, as well as

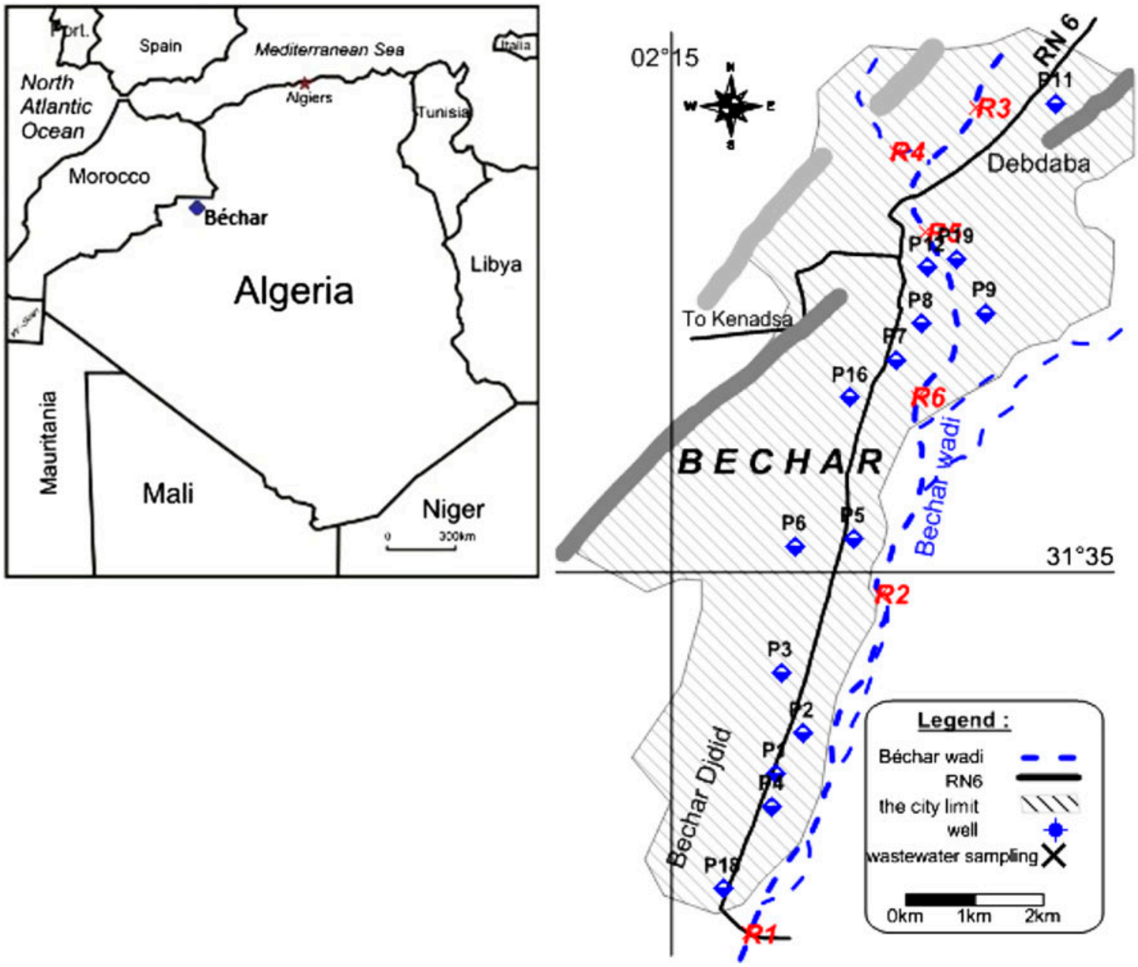


Fig. 1. Location map of Béchar town (SW Algeria) and sampling network.

the possibility of its use to supply drinking water or for other purposes (irrigation, industry, etc.) [13–17]. Sampling was conducted during the months of April 2008 (14 wells) and 2010 (18 wells) (Fig. 1) to identify the mineral composition of Béchar city groundwaters. The parameters analyzed are EC, pH, total dissolved solids (TDS), Eh, O_2, Na^+, Ca^{2+}, K^+, Mg^{2+}, Cl^-, HCO_3^-, NO_3^-, SO_4^{2-}, Mn^{2+}, NH_4^+, I^- B, PO_4^{3-}, and Zn^{2+}. The water characterization was carried out using a graphical and statistical analysis of the physicochemical parameters. The methods described by Rodier [16,18,19] were followed during field and laboratory work. The goal was to ensure that the water samples truly represented the properties and conditions of the subsurface environment. Water was pumped from the well until the temperature, EC, and pH became constant. The collected samples were analyzed for major cations, anions, and TDS. Concentrations of Na^+ and K^+ were determined using a flame photometer. As for Ca^{2+}, Mg^{2+}, HCO_3^-, and Cl^- concentrations, these were determined by volumetric titration method, and SO_4^{2-} and NO_3^- spectrophotometrically. Samples with an error of less than 5% in the cation–anion balance were exclusively used for interpretation; additionally, statistical analysis was carried out using Statistica8 for Windows.

3. Results and discussion

3.1. Identification and classification of facies

The chemical facies representation of Béchar city groundwater in the diagram (Na^+/Ca^{2+}) vs. (Cl^-/HCO_3^-) [18–20] shows the dominance of two characteristics poles (Fig. 2). Both poles are represented by two facies, firstly sodium bicarbonate (2008) and secondly the sodium chloride (2010). A gradual facies transition occurred from 2008 to 2010 sampling. The calcium chloride facies is also present (2010) by four points. The dominance of ions Ca^{2+}, HCO_3^-, SO_4^{2-}, Na^+, and Cl^- [18–20] allowed the representation of the analysis of Béchar city groundwater in the ($Ca^{2+}/HCO_3^- + SO_4^{2-}$) vs. ($Na^+/Cl^-$) diagram (Fig. 3), where the points are concentrated in the calcium sulfate pole with 100% of the 2008 samples, also 50% samples of 2010, and nearly 38% from 2010 are Ca^{2+} Cl^-.

3.2. Contribution of the principal component analysis

Many studies have been devoted to the analysis of chemical data of water through multivariate statistical techniques, among others principal component analysis, they are also used to distinguish between multiple signatures clean groundwater or contaminated, by agricultural activities, mining, and also sewage pollution [6,21–25].

Applying principal component analysis method on Béchar city groundwater has led to the following conclusions (Figs. (4) and (5)):

(1) For the 2008 sampling, the first two axes explain 60.92% of the information contained in the data matrix (Fig. 4). Factor F1 represents 43.86% of the total inertia, it is determined by HCO_3^-, EC, pH, TDS, SO_4^{2-}, Na^+, Ca^{2+}, K^+, Eh, Cl^-, I, B, P, and NO_3^-. The combination of these variables along axis F1 indicates that this factor explains the predominant mechanisms for acquiring mineralization of groundwater in the town of Béchar.

(2) Factor F2 represents 17.05% of the variance expressed, it is determined by the ion NH_4^+ and nutrients, it is a factor characteristic of nitrogen pollution, mainly due to sewage presence. The groundwaters of the city are

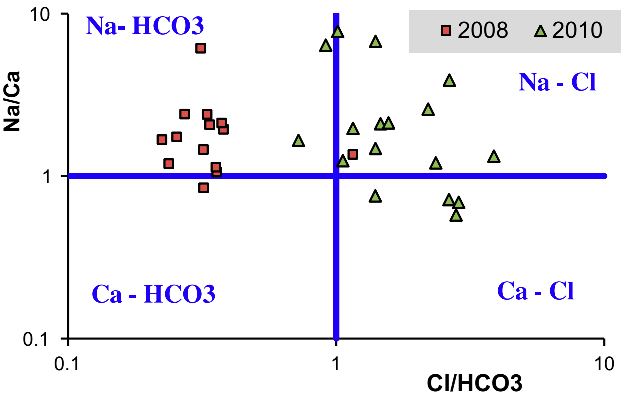


Fig. 2. Report (Na^+/Ca^{2+})—(Cl^-/HCO_3^-).

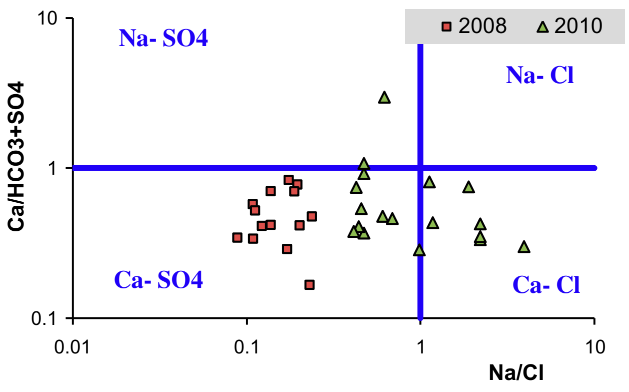


Fig. 3. Report ($Ca^{2+}/HCO_3^- + SO_4^{2-}$)—($Na^+/Cl^-$).

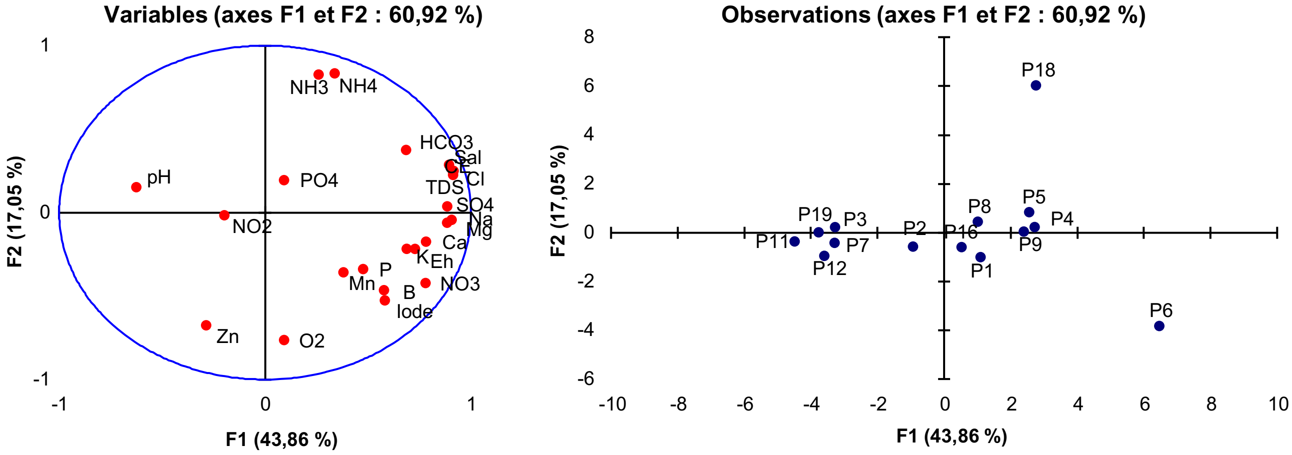


Fig. 4. Factorial plan F1/F2 (2008).

shallow allowing a direct relationship with the wadi water, and ease of movement of organic pollution. The good correlation between the different variables that define the factor F1 reflects a common origin of these ions (Fig. 4). The analysis in the space of the statistical units allows the identification of several groups of water. Also, the mineralization of water from the P18 well is influenced by the presence of NH_4^+ ions, the P6 sample by the NO_3^-, points P8, P5, P4, and P9 by the PO_4^{3-}, wells P3, P1, P7, and P19 by NO_2^-, and then the wells P2, P1, and P16 by mineralization related to their recharge (Cl^-, SO_4^{2-}).

For the 2010 sampling (Fig. 5), the first two axes F1 and F2 explain 59.82% of the overall information; the factor F1 represents 44.04% of the variance, it is determined by Cl^-, Eh, Mg^{2+}, Na^+, HCO_3^- and NO_3^-, the combination of these variables along axis F1 indicates that this factor explains the acquisition of mineralization of these waters; the Factor F2 represents 17.05% of the variance expressed, it is determined by the ions K^+, SO_4^{2-}, NO_2, O_2, and nutrients; it is the factor of mineralization shallow waters mainly due to the presence of oxygen.

The correlation between the different variables that define the factor F1 indicates a possible common origin of these ions; knowing that the grouping of analyzed water is identified by the analysis in the space of statistical units, we can say that the mineralization of water wells P19 is influenced by the presence of NO_3^- ions implying an anthropogenic input. The sample P21 is characterized by the O2, the P16, P3, and P8 by the K^+ and SO_4^{2-}, and wells P3, P18, P4, P6, P5, P1, P19, and P21 by a mineralization linked to traversed geological formations (Cl^-, Na^+, HCO_3^-, and Ca^{2+}).

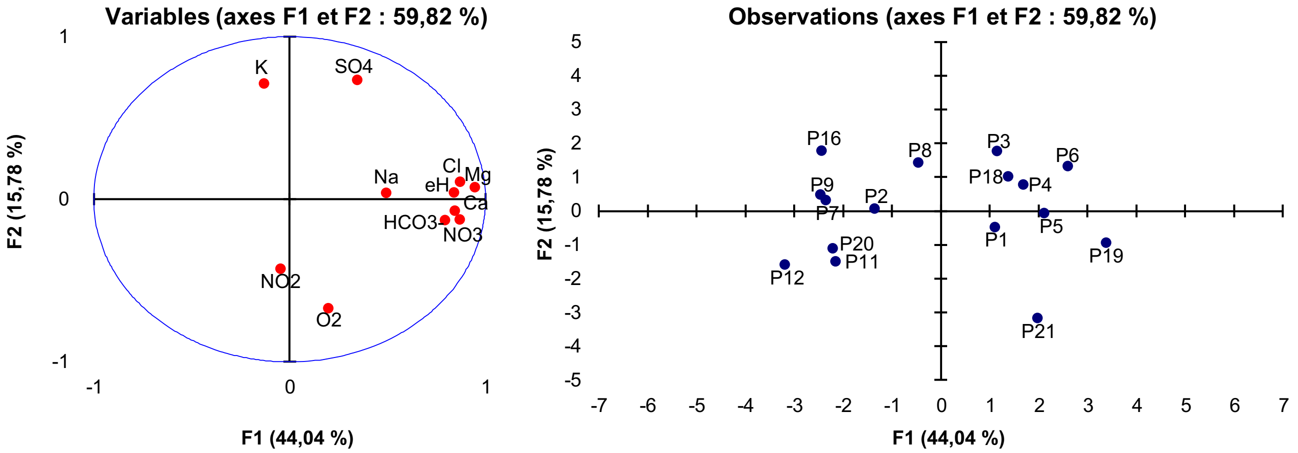
3.3. *Gibbs diagram (1970)*

The Gibbs diagram enables us to determine the different origins of the chemical elements from the correlation established between them, including the geological origin. This is explained by the wells recharge under the effect of the refill by the rainfall and contact wadi/groundwater. There is a change between the two periods, with increased concentrations of chemical elements Ca^{2+}, Na^+, Cl^-, and HCO_3^-, during low water due to evaporation [6,26–29].

Application of Gibbs diagram (Table 1 and Fig. 6) leads to certain conclusions:

(1) For the graph: $Na^+/Na^+ + Ca^{2+} = f$ (TDS), where the origin of Na^+ compared to Ca^{2+}, for the majority of samples is the interaction water/rock (38% for 2010 and 100% in 2008), the remaining 62% of 2010 samples are divided into two groups, the first originates from the evaporation of shallow water, and the second from evaporation of water from precipitation.

(2) The graph $Cl^-/(Cl^- + HCO_3^-) = f$ (TDS) describes the origin of Cl^- compared to the HCO_3^-, which is for the majority of wells, mainly, the interaction water/rock (50% for 2010 and 64% in 2008), while 37% (2010) and 21% (2008) are from shallow water evaporation, and the remainder, namely 14% (2008) and 12% (2010) are from water evaporation precipitation.


Variables (axes F1 et F2 : 59,82 %)

Observations (axes F1 et F2 : 59,82 %)

Fig. 5. Factorial plan F1/F2 (2010).

Table 1
Chemistry origin of Béchar city groundwater according to Gibbs diagram (1970)

Classes	Diagram: Na/Na + Ca			Diagram: $Cl/(Cl + HCO_3)$			
	2008	2010		2008		2010	
Rock dominance	All samples	6.4.8.2.1.3	**37.5%**	4.9.2.16.1.7.8.12.11	**64.2%**	9.8.7.20.11.2.16.12.	**50%**
Evaporation dominance	–	19.10.18.5.21	**31.2%**	6.18.5	**21.4%**	18.6.21.19.5.4	**37.5%**
Evaporation of rainfall dominated waters	–	7.16.20.11.12	**31.2%**	18.3	**14.2%**	1.3	**12.5%**
Rainfall dominance	–	–	–	–	–	–	–

Note: Bold value indicates the percentage from all samples.

3.4. Reporting features

The use of reporting features, in meq/L, can be an indicator of the water quality. The study of the most common features reports used in hydrogeochemistry, to specify the origin environment of groundwater and compare their chemical elements concentration [6,30,31].

3.4.1. Report rSO_4^{2-}/rCl^-

The use of report rSO_4^{2-}/rCl^- [6,20,25] indicates that groundwater samples from the town of Béchar are chlorinated (Fig. 7). This ratio is less than 1 for 92.95% (2008) and 77.77% (2010) of the samples analyzed; therefore, there is a predominance of chlorides on sulfates which can be explained by the leaching of marl gypsiferous in hydraulically upstream.

The graph in Fig. 7 shows that the anthropogenic input in ions SO_4^{2-} and Cl^- is 21.21% of water wells, in 3% points, mineralization is due to water–rock interaction, conditioned by the relatively long residence time of water in this environment. Finally, in 75.73% of cases, mineralization is due to leaching of gypsiferous marly formations by rainwater infiltration.

3.4.2. Report rNa^+/rCl^-

The presence of these two chemical elements (Na and Cl) in natural waters are often related to the dissolution of halite. The evolution of Na^+ is studied as a function of chloride contents because it is considered as stable and conservative tracer evaporites, very soluble, rarely entering in the salt precipitation, not involved in the redox processes and low influenced by the intervention of bacteria. In addition, its movement is not delayed in water [6].

The graphical representation of the evolution of the sodium contents based on chloride concentrations on a logarithmic scale [2,6,23–25,27,30] (Fig. 8), allows us to observe four acquiring process of Na^+ and Cl^- ions: by dilution, human input, interaction water/rock and enrichment by evaporation. In cases where the correlation between Na and Cl ions is significant, this

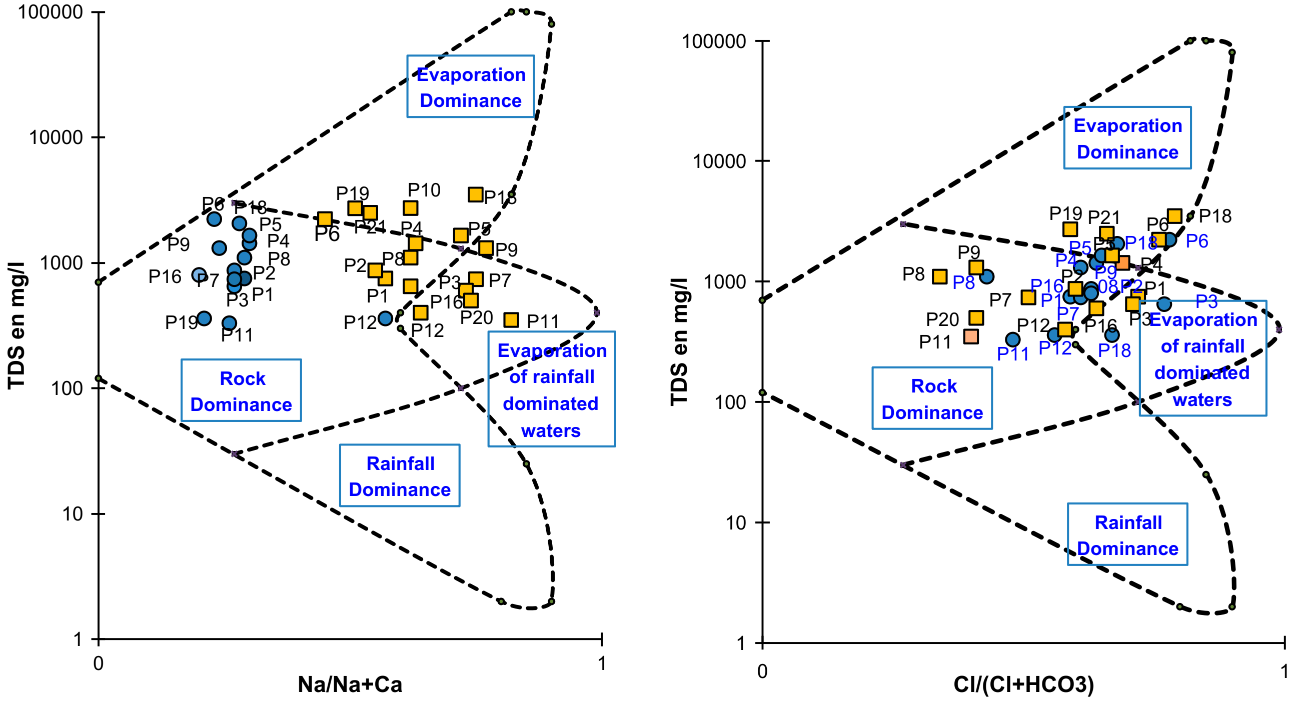


Fig. 6. Various chemical elements origin in Béchar city groundwater (2008, 2010) (Gibbs plot 1970).

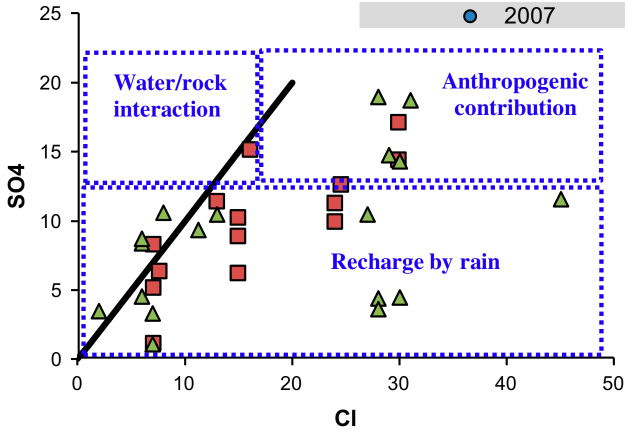


Fig. 7. Report evaluation rSO$_4^{2-}$/rCl$^-$.

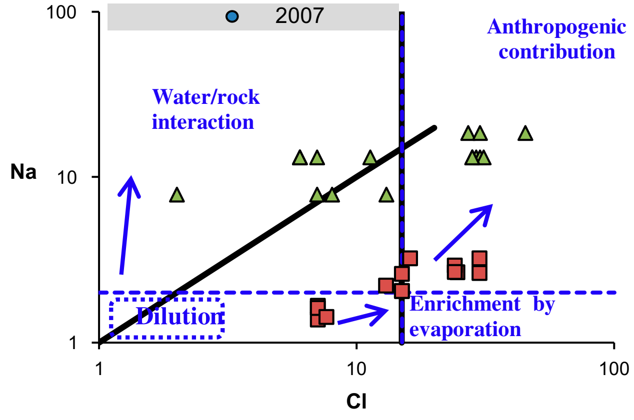


Fig. 8. Na$^+$ and Cl$^-$ origin.

indicates a common origin, which is the halite dissolution in the groundwater transition [30]. The anthropogenic contribution is 58.62% of the wells tested, while the water–rock interaction is 24.13%, and the enrichment by evaporation is around 17.24%. The few points with low chloride concentration, lower to15 meq/l, and an excess of sodium levels in relation to the slope 1, can be explained by the existence of another source for sodium ions, which actually increase the concentration of sodium. This additional contribution could come from the weathering of clay formations, given the fact that the excess Na$^+$ is accompanied by a deficiency of Ca^{2+} to HCO$_3^-$ and SO$_4^{2-}$ (Fig. 8). The increased levels of Na$^+$ cannot be explained by base exchange related to clay minerals which set a Ca^{2+} ion, after release two Na$^+$ ions [24]. This ratio is less than 1 for 82.76% of the water samples analyzed; this can be explained by the deposition of salts in specific climatic conditions, low rainfall and enrichment by evaporation or by leaching of clay soil by recharge water, or by anthropogenic inputs such as discharges.

3.4.3. *Correlation between* $Ca^{2+}/(HCO_3^- + SO_4^{2-})$ *and* Na^+/Cl^-

An examination of the calcium origin vs. the bicarbonates and sulfates can highlight key exchange base exerted in the water–rock and identify the two main sources of Ca^{2+}, namely carbonates and gypsum [20,32,33]. The ion exchange with the rock matrix also controls the calcium content in the groundwater of the city of Béchar (Fig. 9); in case the residence time is relatively long and where the carbon dioxide content is low, and a low water aggressiveness. A decrease in the calcium content compared to $HCO_3^- + SO_4^{2-}$ is a decrease of Na^+ relative to Cl^-, which implies a high concentration of HCO_3^- and SO_4^{2-}. This situation is frequently encountered by the dissolution of evaporitic sedimentary rocks, including gypsum ($CaSO_4{\cdot}2H_2O$) [6,24]. The projection of the points on the graph $Ca^{2+}/(HCO_3^- + SO_4^{2-})$—$Na^+/Cl^-$ (Fig. 9) shows that 20% of water points undergo base exchange with a relatively long residence time, 3% points are in there natural state and 7% have an Ca^{2+} ions excess compared to HCO_3^- and SO_4^{2-}, probably due to gypsum formations that provide more Ca^{2+} ions that can consume the effect of chemical precipitation or effect of calcium binding by clays [24].

3.4.4. *Report* rNO_3^-/rCl^-

The correlation between chlorides and nitrates (Fig. 10) [6,34] indicates the dominance of chlorine on the nitrate, because 100% of the points are below the 1:1 rights, where we note that 32.14% are in anthropogenic input field, 51.72% brought by denitrification loss, or addition of Cl^- meteoric, or recent recharge, and only 3% of the points are located in the natural environment, the presence of NO_3^- in these waters suggests a mixture of two waters, a Cl^- rich one and the other contains some concentration of NO_3^- [6].

3.5. *Origin of chemical elements and identification of anthropogenic inputs*

The acquisition of the chemistry of groundwater in the town of Béchar is governed by several parameters [1,5,35]:

1. The aquifer where the wells are located: the wells taken into consideration, for the evaluation of the chemical quality of Béchar city groundwater, are located as follows:

    (a) P11 in the limestone.
    (b) P20 in the old quaternary.
    (c) P12, P19, P9, P8, P7, P16, P21, and P6 in the recent quaternary and gypsiferous marls.
    (d) P5, P3, P2, P1, and P4 interbedded Carboniferous sandstones with marls and clays.
    (e) P18 in the inferoflux, and end, P22 in alluvium in contact with the Namurian.

2. The distance between the wells and the discharge point (in the wadi).
3. The residence time of the water in the aquifer.
4. The feeding flow direction (hydraulic gradient).
5. The geological formations crossed by water before arriving at the well.
6. The power flow during the rainy period.
7. The hydrochemical evolution is influenced by hydrodynamics wells, due to evaporation (low water period), and under the effect of recharge by rainfall (during high water) [24].

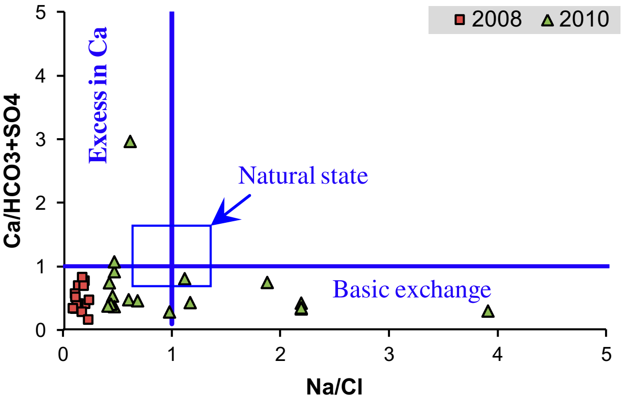


Fig. 9. Basic exchange.

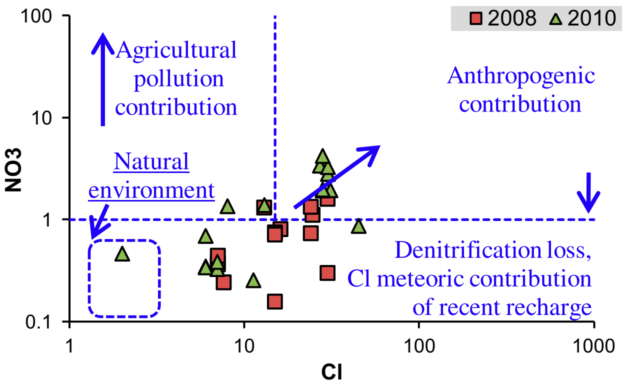


Fig. 10. NO_3 origin.

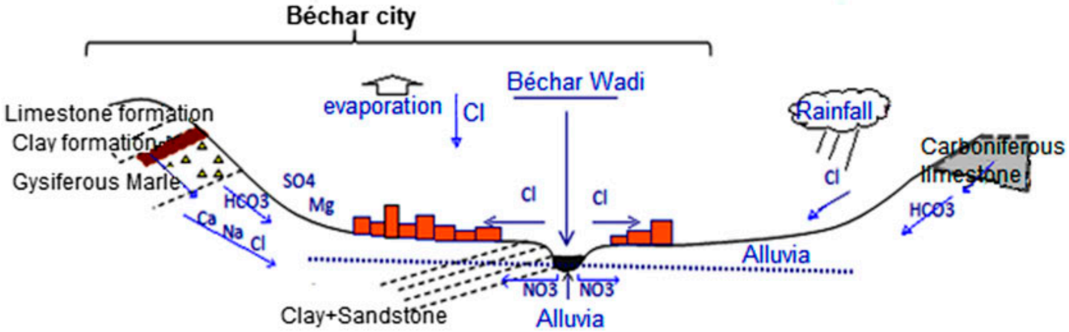


Fig. 11. Acquisition mechanism of chemistry groundwater in Béchar city.

(8) The anthropogenic contribution is also significant source of chemical ions (NO_3^-) [31,36].

We can describe the mechanism of acquisition of the chemistry of Béchar city groundwater (Fig. 11) by the movement of chemical elements such as $HCO_3^-$and Ca^{2+} from Carboniferous limestone formations, and $SO_4^{2-}$and Mg^{2+} ions from sandstone and clay formations, Na^+ from gypsiferous and marly formations, the Cl^- comes from several origins: the Béchar wadi, evaporation, and marley and gypsum formations, the NO_3^- comes from wastewater of the wadi. The mechanisms are primarily activated by leaching, residence time, and basic exchange.

4. Conclusion

This study investigated the physicochemical properties of the Béchar city aquifer to understand the status of water quality and also to detect the sources of contamination. The representation of data on chemical facies classification diagrams allows that analyzed samples are arranged in a calcium sulfate facies and bicarbonate sodium facies (during 2008), and two categories for the analyzed samples during 2010, which are chloride sodium and calcium chloride. This classification is probably due to the variation of the feed stream (rainiest year during 2008). Some chemical ions are from anthropogenic input origin, mainly the nitrates. The chemistry of groundwater in the city of Béchar can be explained by a mechanism of acquisition rather complex, resulting in the movement of chemical elements such as HCO_3^- and Ca^{2+} from Carboniferous limestone formations, and the ions SO_4^{2-} and Mg^{2+} from sandstone and clay formations, Na^{2+} from gypsiferous marly formations, the chloride comes from several sources, either releases of the wadi (anthropogenic), evaporation, marl and gypsum formations, or carbonate formations; the most likely source of NO_3^- is wastewater of the wadi; leaching, time stays, and base exchange are the main actions that activate the chemical elements acquisition mechanism.

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