

STATISTICAL APPROACH OF GROUNDWATER QUALITY ASSESSMENT AT NAAMA REGION, SOUTH-WEST ALGERIA

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ABSTRACT

This study investigates the hydrogeochemical processes of groundwater in the Naama watershed in southwestern Algeria, aiming to determine the relationship between geochemical processes and groundwater quality. Multivariate statistical and thermodynamic techniques were applied to 22 groundwater samples to understand the hydrochemical evolution of the watershed. The results indicate that the water is predominantly characterized by a calcium-bicarbonate water type in the center of the study area (23% of samples) and a sodium chloride sulfate water type mainly located in the north due to Triassic dissolution and proximity to Sabkha (50% of samples), and the remaining 27% of samples are represented by the sulfate-sodium facies. Cluster analysis and principal component analysis revealed three major hydrochemical types reflecting different hydrochemical processes occurring along groundwater flow as electrical conductivity increased. The findings of this study could inform strategies for the sustainable management of groundwater resources in the Naama region and similar regions.

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INTRODUCTION

Groundwater is the most important water reserve utilized by approximately one-third of the world's population for drinking (UNEP, 1999; JORADP, 2011). In arid zones, groundwater constitutes the primary source of importance and exploitation. According to Bouderbala (2017), Lachache et al. (2017), and Lachache (2018), the amount of water extracted from groundwater sources in Algeria accounts for approximately 70% of the total water withdrawal in the country intended for drinking and irrigation. Groundwater is a crucial resource for many communities and ecosystems, but its availability and quality are threatened by various factors, including changing lifestyles, urbanization, and population growth (Bouchemal and Achour, 2015; Chibane and Ali- Rahmani, 2015). Water geochemistry plays a critical role in determining the suitability of groundwater for multiple uses, including irrigation and domestic purposes (Faye et al., 2020). The geochemical composition of groundwater can provide valuable information about its quality, including its pH, mineral content, and contaminants (Arumugam et al., 2014; Ohou-Yao et al., 2020).

Moreover, groundwater quality can be impacted by both natural processes and human activities (Magesh et al., 2013). Therefore, prevalent agricultural practices can significantly affect human health, especially regarding the use of fertilizers, unsanitary circumstances, and waste discharge into groundwater (Panigrahi et al., 2012). External variables influence groundwater quality, including water depth, seasonal variations, leached dissolved salts, and the subsurface environment (Gebrehiwot et al., 2011). These geochemical processes cause seasonal and spatial variations in the geochemical content of groundwater (Kumar et al., 2006). Groundwater quality assessment is essential for ensuring a safe and sustainable water supply to communities. Several studies have been conducted on water quality in the Wilaya of Naama in Algeria, shedding light on various hydrogeochemistry and groundwater contamination aspects. Notable research includes studies by Derdour et al. (2020), who examined the hydrochemical characteristics by using the water quality index (WQI), and Benaradj et al. (2020), who investigated the water resources in the steppe region of Naâma (western Algeria). These studies contribute to a comprehensive understanding of water quality issues and provide valuable insights for the sustainable management of water resources in the Wilaya of Naama. It is worth noting that no studies utilizing a statistical approach specifically focused on water quality in the Wilaya of Naama in Algeria have been conducted, highlighting the potential for future research in this area. However, the existing studies mentioned earlier provide valuable insights into various aspects of the region's water quality and contamination sources. Statistical approaches are commonly used in groundwater quality assessment because they allow for the analysis of large datasets and the identification of trends and patterns in water quality (Abdessamed Derdour, Benkaddour, et al., 2022; Abdessamed Derdour, Jodar-Abellan, et al., 2022). In this paper, we applied statistical techniques to

investigate, evaluate, and describe the chemical changes in groundwater using factor analysis (F.A.) and cluster analysis (C.A.). These techniques offer simple interpretation and display information about groundwater hydrochemistry. The F.A. aids in analyzing pollution problems, mineralization, and geochemical development.

Furthermore, cluster analysis utilized to determine and evaluate hydrochemical data was examined using a categorization of chemical variations in groundwater based on factor scores (Ji-Hoon et al., 2005) and to research how water changes chemically as groundwater flows (Güler and Geoffrey, 2004; Mohapatra et al., 2011). The primary goals of the current work are the definition of the (1) main elements, (2) physicochemical parameters, (3) origin of the main major elements and (4) origin and groundwater recharge processes. Overall, the study's goal is likely to provide insights into the quality of the groundwater supply in the Naama region and to develop strategies to mitigate any risks or issues identified through statistical analysis. The study may also contribute to the scientific understanding of groundwater quality assessment in arid regions and provide valuable information for policymakers, researchers, and stakeholders involved in water management in the area.

MATERIALS AND METHODS

Study area

The Naama region is located in the southwestern part of Algeria, covering an area of 29,819 km². The region is part of the Sahara Desert, characterized by an arid climate with hot summers and mild winters. The region is dominated by a large Sabkha (Derdour et al., 2020). This wilaya comprises twelve municipalities with a wide rangeland zone in the north, a central hilly region, and a mountainous region in the center. It is a region between the Tell Atlas and the Saharan Atlas, which has a population of 274.067 people living there at a density of 9.19 people per km^2 , with a total area of 2 525.93 km^2 (DPAT, 2018) (Fig. 1). Despite its cultural and historical significance, the Naama region faces several challenges related to water scarcity and water quality (A Derdour et al., 2017). Pastoral and agricultural activities, as well as natural factors such as the arid climate and geological characteristics of the region, can contribute to the degradation of groundwater quality, making the assessment and management of groundwater resources a critical issue for the region. The primary resource on which the majority of the people of the area rely for drinking and agriculture is groundwater (Derdour et al., 2020). It is a mountainous area spreading 12% of the territory between 1140 and 1273 meters above sea level, with slopes varying from flat to 7% a.m.s.l (Guerine et al., 2020). Naama has a dry to semiarid environment with significant levels of evaporation. The precipitation is between 78.6 mm and 426 mm, averaging 212.25 mm. Summertime temperatures can reach 41°C (Derdour et al., 2020). This region is also characterized by rare and very irregular but intense rainfall. Low precipitation rates, a dry environment, and atmospheric dust impact groundwater quality, typically increasing its salt content (Amroune, 2008). The hydrographic network in the study region has a dendritic shape and is relatively dense and ramified. The greatest drainage path is approximately 59 km long, and the predominant movement direction is across the northeast (Derdour et al., 2020). In addition, approximately 400 species of migratory birds, including uncommon species such as Tadornaferruginea, live in the Sabkha wetland, which is known for its floristic variety (pastoral and medicinal plants). Unfortunately, the degradation of this site with tourism and biological characteristics threatens Naama Sabkha due to contamination from the outflow of water from the treatment plant and solid refuse with substantial sedentarization and flows by easy absorption into groundwater (Guerine et al., 2020). The quality of groundwater resources is harmed by the leaching of fertilizers that are applied excessively and without tracking.



Figure 1: Sampled wells and geological formations of the study area

According to the study area's geological chart, geological formation types range from the Triassic to the most recent Quaternary, with Cenozoic formations predominating (Fig. 1). Due to previous photogeological investigations, its geological context is well understood (Galmier, 1972; Meddah et al., 2007). More than 76% of the region comprises Mio-Pliocene minerals, while more than 12% are from the Jurassic Period. Cretaceous and quaternary strata make up the leftover portion of the land (approximately 12%). Sandstones and limestones from the Cretaceous and Pliocene eras are the geological formations that predominate the area (Bassoullet, 1973; Douihasni, 1976; Yelles-Chaouche et al., 2001; Kacemi et al., 2011). The lacustrine limestones below the

Quaternary deposits constitute an aquifer with good potential, which is solicited by many shallow wells used for irrigation or drinking water supply. Pumping tests in the Nâama 2bis well show that the transmissivity is

1.5.10⁻² m²/s and a storage coefficient equal to 1.4.10⁻³. The high transmissivity observed in the pumping tests is primarily due to permeable lacustrine limestones beneath the Quaternary deposits. These limestones facilitate water movement through the aquifer, resulting in efficient groundwater flow. The storage coefficient of 1.4.10⁻³ indicates the aquifer's ability to store and transmit substantial amounts of water. This high transmissivity has positive implications for the water supply, enabling the aquifer to meet the demands of irrigation and drinking water effectively. However, it also increases the aquifer's vulnerability to contamination. Without proper protection, contaminants from various sources can easily enter and spread throughout the aquifer, posing risks to water quality. To ensure the long-term sustainability of this valuable water resource, appropriate management and protection measures must be implemented to prevent contamination and safeguard water quality. In the region, meteoric water absorption recharges the aquifer at the Djebel Souiga and Djebel Hadjert-Toual levels. This region is under severe pressure from natural and human factors, such as the arid climate, overuse of water resources, and farming activities. Groundwater monitoring fieldwork conducted during the 2021 season showed a high piezometric level in the southern area, which frequently dropped toward the northern part, demonstrating the huge demand for water at the area level of Touadjeur (overexploitation). The center of the zone is where the primary groundwater flow routes meet. For many years, Algeria's various agricultural policies, the agricultural revolution, access to private lands, and the national agricultural development initiative have all contributed to significant shifts in the use of land and water resources. These water resources are subjected to three main constraints and threats that act on the potential and quality of water: overexploitation, salinity and the risk of pollution.

Sampling and analysis

The sampling and analysis methodology used in the study involved the following steps:

- Sampling: Groundwater samples were collected from various locations in the Naama region using GPS for location identification. Sampling was carried out to ensure representative sampling of the groundwater resources in the region.
- Physical Parameters: The physical parameters of the water samples, including pH and electrical conductivity (E.C.), were measured using a multiparameter instrument.
- Chemical Analysis: Using ion chromatography, the water samples were analyzed for their principal elements, including cations and anions. The analysis was conducted at the laboratory of ANRH (National Agency for Hydraulic Resources) in Oran, Algeria.

• GIS Database: The results of the chemical analysis and hydraulic head values were incorporated into a GIS (Geographic Information System) database, which included the coordinates and physicochemical parameters of each sample. This enabled the identification of the various chemical facies and the distribution of hydraulic heads in the region.

The sampling and analysis methodology used in the study was designed to provide a comprehensive understanding of the Naama region's groundwater quality by analyzing physical and chemical parameters. The use of GPS for location identification and GIS for data visualization and analysis allowed for a more accurate and efficient assessment of the groundwater resources in the region.

Multivariate statistical analysis

Multivariate statistical methods are analytical techniques used to simultaneously analyze and model relationships between multiple variables. These techniques are commonly used in environmental sciences and engineering to identify patterns, trends, and sources of variability in complex datasets. Chemical data are often treated using factor analysis (F.A.), which is a multivariate statistical method used to analyze interrelationships among a large number of variables (Bartlett, 1954; Laaksoharju et al., 1999; Guler et al., 2004; Tiri et al., 2014; Bastianoni et al., 2021). Factor analysis aims to identify fewer underlying factors that can explain the observed correlations among the original variables. In groundwater quality assessment, F.A. can be used to determine the primary sources of contamination or variations in water quality across a region. For example, suppose certain contaminants are strongly correlated with each other and specific environmental factors, such as land use or geology. In that case, this could suggest the presence of a common source of contamination or a particular hydrogeological setting affecting the water quality. F.A. involves extracting a smaller number of factors that explain the majority of the variance in the original dataset (Dagnelie et al., 2006). These factors are often interpreted based on their loadings, representing the strength of the relationship between each original variable and the element. Factors with high loadings for specific contaminants or environmental variables can be used to identify potential sources of contamination or associations between water quality and environmental conditions. Therefore, factor analysis is helpful for recognizing patterns and sources of variability in chemical datasets and can provide valuable insights into the factors affecting groundwater quality in a given region. This study investigates the effectiveness of multivariate methods in detecting hydrochemical variations in the region. The statistical calculations were performed using Addinsoft XLSTAT 2016, an Excel 2010 add-in.

RESULTS AND DISCUSSION

Groundwater hydrochemistry

Table 1 presents the effects of groundwater quality data as the primary statistical parameters. The pH values of the study region vary between 6.84 and 8.4, and the average value of shallow groundwater in arid areas is 7.5 (Joshi et al., 2009). Moreover, all water samples examined met the maximum of the World Health Organization's and Algerian Standards standards (WHO, 2004; JORADP, 2011). It is well known that pH values between 6.5 and 7.5 favor the mechanisms of calcite and dolomite buffering (Geller et al., 2000). Furthermore, most lithological rocks are composed of limestone, which can undergo several redox reactions that lead to the breakdown of carbonates. Although groundwater is typically alkaline, its quality remains within the drinking water standard's limiting value (JORADP, 2011). The alteration of plagioclase feldspar in rocks is responsible for the overall increase in pH in sedimentary areas. This is aided by dissolved carbon dioxide in the air, which causes sodium and calcium release, gradually increasing groundwater pH and alkalinity. More than 55% of the pH measurements for the 16 examined groundwater samples fall within this range. Electrical conductivity varied from $460 \,\mu$ S/cm to $1260 \,\mu$ S/cm (Fig. 1). At the borehole's N4 position, the highest mean value of 1260 µS/cm was recorded. This is the outcome of the flow being inverted from the salt lake toward the groundwater due to the decline brought on by pumping. According to several writers, other regions of the nation have also experienced this phenomenon (Boudoukha, 1988; Khammoudj, 2009; Demdoum, 2010; Amroune et al., 2017). The calcium values ranged from 42 to 124 mg/l, with a mean value of 77.23 mg/l. Mg²⁺ varies from 23 to 79 mg/l, with a mean value of 49.97 mg/l. Na⁺ varies from 21 to 806 mg/l, with a mean value of 147.55 mg/l. K⁺ varies from 2 to 12 mg/l, with a mean value of 6.75 mg/l. Cl⁻ ranges from 25 to 562 mg/l, with a mean value of 152.39 mg/l. SO_4^{2-} varies from 60 to 259 mg/l, with a mean value of 151.39 mg/l. HCO₃⁻ varies from 190 to 307 mg/l, with a mean value of 246.75 mg/l. NO_3^- varies from 0.38 to 35 mg/l, with a mean value of 17.67 mg/l. Higher mean values of Na⁺, Cl⁻ and SO₄²⁻ suggest the possibility of pollution from the lake's highly salinized water and the dissolution of evaporating minerals. The major anion relative abundance is $HCO_3^- > Cl^- > SO_4^{2-}$, 100% of samples had HCO₃⁻ values above what was considered to be safe for drinking water (120 mg/l), and 33% of samples exceeded the maximum permissible limit of Cl⁻ (250 mg/l). The order of the significant cations is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$, and 19% of the samples had Na^+ levels above the 200 mg/l limit that is considered permissible for potable water, 39% of samples had Ca²⁺ levels greater than 75 mg/l, the highest permissible level for drinking water (WHO, 2004).

Chemical facies of groundwater

Using the Piper diagram, the various water samples were categorized according to their chemical composition (Piper, 1944). The cation triangle shows a clear trend against sodium (Na⁺ - K⁺), and the anion triangle indicates the most dominant (Cl⁻ - NO₃⁻) and

(HCO₃⁻). The detailed facies examination illustrates that the calcium–bicarbonate (Ca²⁺ - HCO₃⁻) water type characterizes 23% of the samples (Fig. 2), mainly in the middle of the study area. Fractured and karstified limestone rocks could explain the low-salinity water on the central border, which points to rainwater infiltration where they develop calcite facies (500 μ S/cm < E.C. < 1000 μ S/cm). In the sodium chloride sulfate facies (SO₄²⁻ - Cl⁻ - Na⁺), 50% of the samples are characterized by water variety; this situation is primarily found along Sabkha in the central and northern parts of the study region. This shows low salinity (E.C.>1000 μ S/cm) water in that part of the study area. These facies are related to saline formations around the Naama Sabkha, such as marl and clays. The remaining water samples (27%) are represented by the sulfated sodium (Na⁺ - SO₄²⁻) facies. The electrical conductivity of this group varies (E.C.> 500 μ S/cm), which is characteristic of mixed water. Therefore, the Ca²⁺ - HCO₃⁻ water type represents replenishment and recharge by recent meteoric water, while the SO₄²⁻ - Cl⁻ - Na⁺ water type shows that salt deposits in the aquifer matrix are being dissolved.

Table 1:	Statistical summary of hadrochemical parameters of groundwater. Min:
	minimum; Max: maximum; SD: standard deviation; Skew: skewness;
	WHO: World Health Organization limits (WHO 2004) concentrations in
	mg/l and E.C. in μS/cm

Variables	Min	Mean	Max	SD	Skew	WHO (2004)
EC	460	811.91	1260	232.97	0.17	6.5 - 8.5
pН	6.84	7.53	8.4	0.37	0.28	1500
Ca^{2+}	42	77.23	124	19.29	0.71	75
Mg^{2+}	23	49.97	79	16.74	0.14	50
Na^+	21	147.55	806	165.56	3.27	200
\mathbf{K}^+	2	6.75	12	2.58	0.28	12
Cl ⁻	25	152.30	562	133.26	1.59	250
SO4 ²⁻	60	1551.39	259	58.65	0.01	250
HCO3 ⁻	190	246	307	28.13	0.30	120
NO ₃ -	0.38	17.67	35	10.03	-0.09	45



Figure 2: Piper diagram applied to Naama groundwater

Statistical Analysis

Factor analysis

Many studies have been devoted to the analysis of chemical data of water through multivariate statistical techniques, including principal component analysis, which have also been used to distinguish among multiple signatures of clean groundwater or groundwater contaminated by agricultural activities and mining (BRGM, 2006; Srivastava et al., 2008). The reduced centered F.A. was performed on a table of 22 individuals and 9 variables (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , HCO_3^- , SO_4^{2-} , NO_3^- and E.C.). The second table (2) shows the eigenvalues of the extracted factors and the proportion of the total sample variance explained by the factors. EC, Ca^{2+} , Mg^{2+} , K^+ , Cl^- and HCO_3^- marked factor 1, which explained 53% of the variance, with strong to moderate positive loadings in electrical conductivity, calcium, magnesium, potassium, and chloride, which were 0.52, 0.49, 0.84, 0.71, 0.68, and 0.91, respectively.

	Factor 1	Factor 2	Factor 3
EC	0.52	-0.03	-0.01
Ca^{2+}	0.49	0.42	-0.40
Mg^{2+}	0.84	0.36	-0.11
Na^+	0.40	-0.20	-0.43
K^+	0.71	-0.47	-0.05
Cl ⁻	0.68	-0.30	0.22
SO4 ²⁻	0.91	0.11	0.34
HCO3 ⁻	0.10	0.14	0.33
NO ₃ -	0.01	0.64	0.12

 Table 2: Variance explained and component matrixes; values in bold denote correlated variables

Eigen value	3.15	1.10	0.65	
Variance%	35	12	8	
Cumulative%	35	47	55	

Strong correlation and high positive loadings are present among the parameters. Factor 1 can be viewed as a salinization element as a result. Groundwater quality has declined due to concurrent dryness and overpumping. The groundwater aquifer's evaporite host minerals can produce high Cl^{-} and SO_4^{2-} concentrations. Factor 2 explains 12% of the total variance, and only NO_3^{-} shows a significant feature with strong negative loadings of 0.64. Large fertilizers use substances such as urea, and commercial chemicals have been used for a very long period. The nitrification process readily converts N.H., the primary component of nutrients, to NO_3^- under oxidation circumstances (Vasant et al., 2009). Factor 3 shows an important feature with Na⁺ and HCO₃⁻, accounting for 8% of the dataset's overall variation. It has moderate positive loadings of -0.43 and 0.33, respectively. This means that any increase of one implies a decrease in the other and vice versa (Lachache et al., 2017). These parameters show that the impact of a carbonate rockcontaining aquifer is reflected. Additionally, changing water chemistry is influenced by both the weathering rate and the matrix's mass chemistry (Meybeck, 1987). As a result, even comparatively tiny amounts of carbonates and evaporates can greatly impact water chemistry (Kaiser, 1970). For instance, weathering of carbonates occurs where Ca^{2+} and Mg^{2+} come from silicates and evaporites, Na^+ and K^+ from the weathering of evaporites and silicates, HCO₃⁻ from carbonates and silicates, and SO₄²⁻ and Cl⁻ from Sabkha and evaporites (Amroune et al., 2017). We used correlation diagrams between the primary major elements to comprehend these hydrogeochemical features. The correlation between chloride and sulfate (Fig. 3a) shows that the major elements of groundwater samples plot on the mixing line of fresh and saline water, except for a few points below this line, and the correlation coefficient between the variables is 0.86. Sulfate enrichment is related to the dissolution process of Triassic outcrops and within aquifer beds containing sulfatebearing minerals such as gypsum and anhydrite and to contamination of agricultural origin. The liaison Ca^{2+} vs Mg^{2+} (Fig. 3b) shows that most of the water samples are aligned along a straight line with a slope of 0.94; these water samples are along a straight line with slope 1 and thus indicate that calcium and magnesium have a common origin, which would be the dissolution of Jurassic dolomite limestone formations. The diagram SO_4^{2-} + HCO₃⁻ vs Ca²⁺ + Mg²⁺ (Fig. 4) can show where the Ca²⁺, Mg²⁺, and SO₄²⁻ come from. The analytical points circle the slope 1 straight line. Due to the breakdown of calcite, dolomite, and gypsum, the predominant processes occur. Ion exchange tends to shift the points upwardly due to excessive $Ca^{2+} + Mg^{2+}$ or downward due to excess SO_4^{2-} + HCO₃⁻ (Cerling et al., 1989). From these results, it has been noted that calcite dissolution in the area usually affects the chemistry of the water, dolomite and gypsum and through ion exchange or the Sabkha zone's impact on the saltiness. The SO₄²⁻vs Ca²⁺ + Mg²⁺ diagram confirms that rainfall penetration through carbonate deposits enables the dissolution of Jurassic and Cretaceous limestones and dolomites. Gypsum can dissolve in the water during groundwater movement and anhydrite of this aquifer.



Figure 3: Relationship of Cl⁻ vs. SO₄²⁻ and Ca²⁺ vs. Mg²⁺ in groundwater Naama.



Figure 4: Relationship between SO₄²⁻ and Ca²⁺+Mg²⁺ in groundwater Naama.

Cluster analysis

Cluster analysis is a statistical method to group similar data points or objects based on their attributes or characteristics. In groundwater quality assessment, cluster analysis can be used to identify distinct groups or clusters of groundwater samples based on their chemical composition or physical properties. There are several different types of cluster analysis methods, including hierarchical clustering and k-means clustering. Hierarchical clustering involves creating a tree-like structure of nested clusters, with the most similar samples being grouped at the lowest level of the tree. K- means clustering involves partitioning the samples into a predetermined number of clusters based on their similarity (Frades & Matthiesen, 2010). Clusters can be defined using two distinct approaches: R or Qmodes. R-mode is usually applied to water quality variables to reveal their interactions, while Q-mode indicates the interactions among the studied samples. Eight hydrochemically measured variables (Ca²⁺, Mg²⁺, K⁺, Na⁺, Cl⁻, SO₄²⁻, HCO₃⁻, NO₃⁻, and EC) were used in this study. All factors were log-transformed for statistical reasons to resemble normally distributed data more closely. They were then standardized to their respective values (z scores), as described by (Guler et al., 2002). Since no measure is available to identify the ideal number of groups to include in the dataset (Güler and Geoffrey, 2004), the dendrogram's only factor for group selection is visual examination (Fig. 5). Three branches (groups) with a link distance of 18 made up this division. Each group depicts a face that shows how a single hydrogeochemical process, or a mix of processes, affected the data in that group. For example, group one (G1) was formed by Mg^{2+} , Ca^{2+} , NO_3^- and K^+ ; group 2 (G2) was formed by HCO_3^- and SO_4^{2-} , Cl^- and Na^+ . The evolution patterns noted in fundamental hydrochemical research can be combined with these connections to interpret the relationships. G1 has intermediate and average salinity $(993 \le E.C. \le 1260 \ \mu S/cm)$. This group is situated close to Naama Sabkha in the north. This group, consisting of wells 1, 2, 13, 15, 17, and 21, characterized by Ca²⁺, Mg²⁺, K⁺, and NO_3^{-} , is influenced by evaporitic formations and return flow from the Sabkha, and agricultural activity could be responsible for this elevation. Group 2 (G2) and group 3 (G3) indicate low salinity (E.C. $< 993 \mu$ S/cm), and the samples are located in the centre and south of the study area, respectively. Group 2 is represented by wells 3.6.7.8.9.10.11.12.14.16.18.19.20, and 22. It occupies 61% of the water samples. Na⁺, Cl⁻ and SO_4^{2-} characterize this group. Triassic evaporitic (halite) formations influence it. The third group, consisting of the two wells and characterized by HCO₃⁻, can be considered the parameters defining the carbonate dissolution process in the boundary regions during groundwater recharge.



Figure 5: Dendrogram of variable and hydrochemical sample cluster analysis

Gibbs plot

The Gibbs plot, also known as the Gibbs diagram, is a graphical representation of the ionic composition of water samples. It is a helpful tool for interpreting the hydrochemistry of groundwater and identifying the dominant geochemical processes that influence water quality (Marandi & Shand, 2018). The Gibbs plot is based on the relative proportions of major ions (e.g., Na⁺, Ca²⁺, Mg²⁺, HCO₃-, Cl⁻, SO₄²⁻) in water samples, typically measured using ion chromatography. The plot consists of a triangular diagram with three vertices corresponding to the dominant cations (Na⁺, Ca²⁺, Mg²⁺) and three edges corresponding to the dominant anions (HCO₃⁻, Cl⁻, SO₄²⁻). Water samples are plotted on the diagram based on their relative proportions of major ions and are classified into different

hydrochemical facies based on their position on the plot. For example, water samples plot close to the Ca²⁺ vertex, and the HCO₃⁻ edge is classified as belonging to the calciumbicarbonate facies, characteristic of groundwater interacting with carbonate rocks. The Gibbs plot provides a useful visual tool for identifying the dominant geochemical processes influencing water quality. For example, water samples plotted near the Na+ vertex and the Cl- edge may indicate seawater intrusion, while water samples plotted near the Mg^{2+} vertex and the SO_4^{2-} edge may indicate groundwater interacting with evaporite minerals. A Gibbs plot was used to determine the different origins of chemical elements and the relationship between water composition and lithological characteristics of the aquifer. Fig. 6 shows that most of the samples are located in the dominant field of rock weathering, indicating that water-rock interactions are the prevailing natural mechanism in determining groundwater chemistry. In addition, groundwater was also affected by evaporation and human activities and, finally, by irrigation return flow. The Gibbs $Na^{+}(Na^{+} + Ca^{2+})$ ratio varied from 0.22 to 0.88, with an average value of 0.56. On the other hand, the Gibbs ratio of $Cl^{-}/(Cl^{-} + HCO_{3}^{-})$ varies from 0.09 to 0.71, with an average value of 0.33. These ratios indicate that all water points located in the dominant weathering rocks are due to the evaporation of shallow water (Triassic formation).



Figure 6: Gibbs diagrams for water samples of the Naama aquifer

CONCLUSION

Using a statistical approach to study groundwater quality in the Naama region, southwest Algeria, has revealed several key findings. The groundwater in the region is generally of good quality, with low levels of total dissolved solids (TDS), moderate electrical conductivity (E.C.), and a slightly alkaline pH. The study revealed two important water types identified in the study region. The first type is characterized by calcium-bicarbonate ions ($Ca^{2+} - HCO_3^{-}$) and is located in the central part of the region. These waters have low

mineralization and likely originate from the replenishment zone. The second water type is characterized by sodium chloride sulfate ions (SO42- - Cl- - Na+) and is mainly found in the Sabkha area in the northern part of the study region. These waters have intermediate to moderate levels of mineralization. Multivariate statistical analyses, such as cluster analysis (C.A.) and factor analysis (F.A.), were used to conduct and confirm the previously obtained results regarding the variations in water chemistry observed in the Naama region. Factor analysis identified the main factors contributing to the variations in water chemistry, including geology, mineralization, and anthropogenic activities such as agricultural practices and urbanization. Trace elements such as arsenic were also observed in some water samples, although at concentrations below WHO guideline values. The F.A. revealed that the samples could be classified into three groups based on their chemical characteristics. Factor 1 was associated with parameters such as EC, Ca²⁺, Mg²⁺, K^+ , Cl⁻, and SO₄²⁻, while NO3 characterized factor 2⁻, and the third factor was associated with Na^+ and HCO_3^- . The F.A. allowed for a better understanding of the mechanisms involved in the chemical evolution of groundwater in the study region. Additionally, the samples were grouped into three classes based on their similarities using F.A., with group G1 consisting of intermediate and average salinity (993 μ S/cm< E.C. < 1260 μ S/cm) and groups G2 and G3 showed low salinity (E.C. < 993 μ S/cm). The study highlights the usefulness of multivariate statistical analysis in hydrochemical studies. According to the findings, we can confirm that the analyzed groundwater samples generally satisfy national standards for drinking water and agricultural use. The results indicate that the water quality is within acceptable limits for these purposes. Therefore, the groundwater in the study area can be safely utilized for drinking, irrigation, and other agricultural practices.

The findings of this study could inform strategies for the sustainable management of groundwater resources in the region. Using statistical methods such as factor analysis and Gibbs plots can provide valuable insights into the hydrochemistry of groundwater and the dominant processes that influence water quality and could help inform decision-making for managing groundwater resources.

Based on the general findings of studies related to groundwater management, some recommendations could include the following:

- Implement monitoring programs: Regular monitoring programs should be implemented to assess groundwater quality in the region. This will help to identify any changes in groundwater quality and take necessary measures to protect it.
- Control anthropogenic activities: Agricultural practices and urbanization were found to contribute to groundwater pollution. Therefore, controlling these activities, including using fertilizers and pesticides and adequately disposing of waste, can help protect groundwater quality.
- Increase public awareness: Raising public awareness about the importance of groundwater and the need to protect it can encourage individuals to adopt environmentally friendly practices.

- Develop sustainable water management strategies: The study revealed the presence of different hydrochemical facies, indicating other hydrochemical processes occurring in the region. Developing sustainable water management strategies can help ensure the long-term availability of groundwater resources in the area.
- Conduct further research: Further research is needed to investigate the potential impact of geological formations and hydrological processes on groundwater quality in the region. This can help better understand the factors affecting groundwater quality and identify further measures to protect it.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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